American Chemical Society
42nd Middle Atlantic Regional Meeting
at the University of Maryland, College Park, Maryland

MARM 2011
International Year of Chemistry

www.marmacs.org/2011
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Participating MARM ACS Sections
(Representing Over 30,000 Members)

Washington DC (Host of MARM 2011)
Dealaware (Host of MARM 2010)
Lehigh Valley
Maryland (Host of MARM 2012)
Monmouth County
   New York
   New Jersey
   Philadelphia
   Princeton
Ocean County
South Jersey
Southeastern Pennsylvania
Susquehana Valley
   Trenton
Western Maryland
42nd Middle Atlantic Regional Meeting

Welcome from the Chemical Society of Washington and the University of Maryland

On behalf of the MARM 2011 Organizing Committee, the Chemical Society of Washington, founded in 1884 and established in 1893 as the Washington Section of the American Chemical Society, and the University of Maryland, College Park, the largest university in the Greater Washington area, we are pleased to welcome you to the 42nd Middle Atlantic Regional Meeting, MARM 2011. This is the International Year of Chemistry, and with this theme we are happy to host this meeting near the capital of this nation with its focus on international activities, the national office of the American Chemical Society with its outreach to the chemical sciences throughout the world, and the University of Maryland with all of its international linkages.

Twenty-two symposia are included in this year’s technical program, and there are more than 300 contributed papers. Speakers have come from institutions in the United States and internationally. Symposium topics have the flavor of international activities, and one of them, “Redefining the Kilogram and Avogardo’s Number,” promises to have far reaching consequences for chemistry internationally. You will find symposia that take advantage the enormous talent that we have in the Greater Washington Area that is rich in national laboratories, universities, and developing chemical technologies.

MARM 2011 begins on Saturday, May 21st with a focus on research and education. The high school teacher program will be on that day as will the high school awards luncheon. The first of two full days of poster presentations occur on Saturday alongside the opening of the Exhibitor Booths. Join us on Saturday evening for a reception and refreshments to meet colleagues and friends. On Sunday, symposia continue with emphasis on careers in the morning and Plenary addresses by distinguished international experts on major issues that confront the international chemical community: energy, diseases, and climate change. Join us and ACS Directors for an ice cream social following the Plenary addresses with ice cream from the world renowned Maryland Dairy. Monday continues the technical program and is the second full day for poster presentations. The evening has the Awards Banquet that will be joint with the monthly meeting of the Chemical Society of Washington, and ACS President-Elect Bassam Shakashiri will be the featured speaker. Tuesday morning completes the 2011 MARM program, and allows participants time to visit the campus and the many museums and activities in the Washington, DC area.

We are fortunate to have such generous sponsors, and we are grateful for their contributions. Thanks also to our exhibitors and advertisers, all of whom are listed on the following pages. This meeting would not have been possible without the tremendous effort of the organizing committee and all of the volunteers who give their time and energy.

Yours truly,
Michael P. Doyle
General Chair, MARM 2011
Welcome Letter from President Loh to Participants of the 2011 Middle Atlantic Regional Meeting of the American Chemical Society

Welcome to the University of Maryland and to the 2011 Middle Atlantic Regional Meeting of the American Chemical Society. We are pleased that our university was selected as the site for this important meeting during the International Year of Chemistry. I am proud that the president-elect of the American Chemical Society, Professor Bassam Shakashiri, is a graduate of the University of Maryland.

Chemistry was one of the first academic departments established at the University of Maryland, founded in 1859 and today its faculty are leaders in advancing our science and technology agenda. In addition its robust research profile, the University of Maryland has gained a reputation for strength in entrepreneurship and innovation. These elements are vital to the success of higher education in the 21st century.

The greater Washington area has one of the world’s greatest accumulations of scientific talent and resources, and we are happy to be an integral partner in developing the region’s scientific and educational base. Our proximity to our nation’s capital and the headquarters of the American Chemical Society gives us a special advantage. I hope that you will take this opportunity to visit Washington, DC and experience some of its attractions. I invite you to visit the classrooms, laboratories and artistic venues on our campus. I wish you an enjoyable visit and a productive, stimulating meeting.

Sincerely,

Wallace Loh
President
Dear Middle Atlantic Regional Meeting Participants:

On behalf of the more than 163,000 members of the American Chemical Society, I am pleased to extend greetings to the attendees of the 42nd Middle Atlantic Regional Meeting (MARM 2011) at the University of Maryland, College Park, Maryland.

I am especially pleased that Professor Michael Doyle, General Chair, and the MARM organizers have selected “International Year of Chemistry” as the theme for this event – this is our chance to increase the public appreciation of chemistry, to encourage interest in chemistry among young people, and to generate enthusiasm for the creative future of chemistry. Technical programming and topical symposia emphasize Life Sciences, Materials Sciences, and Chemical Education. Please take this opportunity to interact with your colleagues and to discuss developments taking place in your field.

While you’re here, I do hope that you are able to take the opportunity to fully explore the interesting complement of symposia, workshops, and special sessions, attend the many social events, visit the exhibits, and take advantage of the greater Washington, DC and Baltimore, Maryland area’s many attractions.

I am grateful to the organizers and many volunteers, especially our host, the Chemical Society of Washington Section of the ACS, the MARM Steering Committee, and the other 15 participating sections of the Middle Atlantic Region – representing almost 28,000 members – for their hard work and dedication to create an intellectually stimulating and personally enjoyable experience here in College Park.

Sincerely,

Nancy B. Jackson, Ph.D.
President
American Chemical Society
A MESSAGE FROM GOVERNOR MARTIN O’MALLEY

Dear Friends,

It is my pleasure to welcome you to the University of Maryland for the 42nd Annual Middle Atlantic Regional Meeting 2011 hosted by the Chemical Society of the Washington Section of the American Chemical Society.

As we make the turn into the global 21st century economy, we must continue to spur innovation throughout our state by strengthening our greatest asset—the ingenuity of our people and the diversity of our industries. Through partnerships and shared ideas, we will be able to grow our diverse middle class, improve technology and education, and foster a thriving economy.

As you take the next few days to celebrate scientific innovation and exchange ideas and knowledge, we hope you have time to enjoy our wonderful state inclusive of our beautiful Chesapeake Bay, our historic towns and national sites, our diverse urban centers, and our expansive ocean coast. All are easily available due to our compact size and unique landscape.

Because of your dedication to the pursuit of a greater tomorrow, we move closer each day to solving some of our greatest challenges and enhancing the well-being of future generations. On behalf of all Marylanders, I thank you for your continued commitment to our friends and families. Please accept my best wishes for a successful and enlightening event.

Sincerely,

Martin O’Malley
Governor
April 21, 2011

Members of the
Middle Atlantic Region
Chemical Society of Washington

Dear Distinguished Members:

On behalf of the City of College Park, I want to extend to each of you my sincere welcome to the 42nd Annual Middle Atlantic Regional Meeting.

In addition to what appears to be a full agenda of symposia for the “International Year of Chemistry”, I hope you will have the opportunity to experience the community of College Park.

Beyond the busy pace of Route 1, the city’s “Main Street,” there are 12 distinct residential neighborhoods that help to create the overall atmosphere of a small town. Families take advantage of neighborhood playgrounds, a skating rink, athletic fields, swimming pools, a community center, and Lake Artemesia. An evolving series of hiker-biker trails links many of those amenities to each other and to the University.

A significant chapter in early aviation history began in 1909 in College Park at what is the world’s oldest continuously operating airport. Wilbur Wright trained military officers to fly the government’s first airplane there, and the first Army Aviation School was established there in 1911. Today, The College Park Aviation Museum, located adjacent to the airport, depicts the role of the College Park Airport in many firsts of American flight.

Once again, welcome to the City, and please accept my best wishes for a stimulating and fruitful annual meeting!

Sincerely,

Andrew M. Fellows, Mayor
City of College Park

Home of the University of Maryland
May 21, 2011

Dear Friends:

I want to extend a warm welcome to everyone attending the American Chemical Society’s 42nd Middle Atlantic Regional Meeting. For more than 100 years, the American Chemical Society (ACS) has been a national leader in the field of chemistry. From organizing professional networks and information sharing, to hosting educational and professional gatherings, ACS is committed to supporting scientists within the chemical community.

This year’s theme is “International Year of Chemistry,” and it is an important opportunity to show members of the ACS what Maryland has to offer. I am proud that Maryland has become a national leader in the sciences. Maryland is home to our nation’s premier research facility, the National Institutes of Health, as well two of the finest academic medical centers in the world—Johns Hopkins University and the University of Maryland Medical Centers. Our state ranks 4th in the nation in biotechnology and I am confident that it will continue to grow.

Again, welcome to the ACS’s 42nd Middle Atlantic Regional Meeting and best wishes for a successful and productive conference.

Sincerely,

Benjamin L. Cardin
United States Senator
Dr. Michael Doyle, Chair  
Department of Chemistry & Biochemistry  
University of MD, College Park  
College Park, Maryland 20742-0001  

Dear Dr. Doyle & Friends:  

Greetings to the members and guests of the Chemical Society of Washington on the occasion of your 42nd Annual Middle Atlantic Regional Meeting: "International Year of Chemistry". Thank you for the kind invitation to share this prestigious event with all of my good friends from the chemical science community. I know that your deliberations will be cutting-edge and simulating for everyone who attends.  

Chemistry is about exploration, discovery and innovation. It is an intellectual and practical incubator for new ideas and new technologies. The future of our economy and our nation will depend upon our ability to innovate and to win market share. The new ideas and new technologies which you will discover will lead to the jobs of tomorrow for Maryland and for America.  

In my role as Chair of the Commerce, Justice, Science Appropriations Subcommittee, I am critically aware that in order to stay competitive our country must continue to invest federal dollars in science and technology as well as technological education. This investment will help create high-paying, high-skill jobs that will preserve our nation’s leadership in the global 21st century economy. Rest assured I will always fight to secure robust funding for our nation’s scientific programs at facilities such as NIH, NIST, FDA and the NSF.  

Perhaps, together we can rekindle the spirit of exploration and discovery that defines our nation and its people.  

Sincerely,  

Barbara A. Mikulski  
United States Senator
American Chemical Society
1155 Sixteenth Street, NW
Washington, DC 20036

Dear Friends,

It is my pleasure to welcome you to the great State of Maryland for your 42nd Middle Atlantic Regional Meeting (MARM). Events such as these serve a vital purpose as they provide a terrific opportunity to learn, to share and to talk about issues in the field that are of benefit on a global scale. This event will also showcase the advantages that the Maryland area offers.

The theme of this year’s meeting, “International Year of Chemistry,” exemplifies your mission to advance the broader chemistry enterprise and its practitioners for the benefit of the Earth and its people. Since it was founded in New York on April 6, 1876, the American Chemical Society has held true to that mission by helping to promote the advancement of chemistry research and education.

Through your leadership you have been able to address the needs of research and advancement in the ever evolving field of chemistry. May you leave today’s meeting feeling empowered and enthusiastic about your future endeavors. Your good work continues to be a great contribution to our region, to the nation and to the world.

Wishing you a very successful and productive event. With kindest regards, I am

Sincerely yours,

STENY H. HOYER

NOT PRINTED AT TAXPAYER EXPENSE
Greetings

The Chemical Society of Washington
Section of the American Chemical Society
42nd Middle Atlantic Regional Meeting
"International Year of Chemistry"

May 21 - 24, 2011

As Mayor of the District of Columbia, it is my pleasure to extend warm greetings to the Chemical Society of Washington Section of the American Chemical Society on the occasion of your 42nd Middle Atlantic Regional Meeting (MARM 2011).

The American Chemical Society's mission "to advance the broader chemistry enterprise and its practitioners for the benefit of Earth and its people" is to be commended. I would like to take this opportunity to thank the participating scientists, students, and teachers for their dedication and commitment to academic and professional excellence in the field of chemistry. As you gather to reflect on your accomplishments and discuss new ideas, I invite you to visit the monuments, museums, and diverse neighborhoods that make this city so enriching.

On behalf of the residents of the District of Columbia, you have my best wishes for an enjoyable and productive event.

Vincent C. Gray
Mayor, District of Columbia
ACS Board of Directors

Members of the Board of Directors Expected to be at MARM 2011
(Join us for the ice cream social that follows Plenary Lectures on Sunday, May 22nd)

Bassam Z. Shakhashiri, President-Elect

University of Wisconsin
Bassam Z. Shakhashiri is a chemistry professor at the University of Wisconsin-Madison. He received his A.B. from Boston University in 1960, his M.Sc. from the University of Maryland in 1965 and his Ph.D. in 1968. He is the first holder of the William T. Evjue Distinguished Chair for the Wisconsin Idea at the University of Wisconsin-Madison, where he has been a professor since 1970. He has been a member of the American Chemical Society since 1961.

Pat N. Confalone

Director, District III
Pat N. Confalone is vice president at DuPont, Global Research & Development, Crop Protection. He earned his Bachelors Degree from Massachusetts Institute of Technology in 1967, Masters Degree from Harvard University in 1968, Ph.D. from Harvard University (R. B. Woodward) in 1970, and Post-Doc at Harvard University (R. B. Woodward) in 1971. He has been a member of the American Chemical Society since 1967.

Dennis Chamot
Dennis Chamot is the Associate Executive Director of the National Research Council, Division on Engineering & Physical Sciences. He earned his Bachelors and Masters Degrees at Polytechnic University in 1964. He earned his Ph.D. at the University of Illinois in 1969, and his M.B. A. from the University of Pennsylvania, Wharton School in 1974. He has been a member of the American Chemical Society since 1964.

Marinda Li Wu

Director-At-Large and Candidate for ACS President-Elect
Marinda Li Wu is founder and president of Science is Fun! She earned a Bachelors Degree at the Ohio State University in 1971, and Ph.D. from the University of Illinois in 1976. She has been a member of the American Chemical Society since 1970.

Valerie J. Kuck

Director-At-Large
Valerie J. Kuck is an Adjunct Professor at the College of St. Elizabeth Chemistry Department. She earned her Bachelors degree at St Mary of the Woods College in 1961, and her Masters degree at Purdue University in 1965. She has been a member of the American Chemical Society since 1964.

Neil D. Jespersen

Director, District I
Neil D. Jespersen is a Professor at St. John’s University. He earned his Bachelors Degree at Washington & Lee University in 1967, and his Ph.D. at Pennsylvania State University in 1971. He has been a member of the American Society since 1968.
2011 Mid-Atlantic Regional Meeting
May 21-24, 2011

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Webmaster
Paul Tukey (Bell Labs)

ACS Office of Regional Meetings
Michelle Stevenson (ACS)
Kimberly Savage (ACS)
MARM 2011 Volunteers

This regional meeting would not have been possible without the invaluable efforts of the volunteers – session chairs and moderators, workshop leaders, event organizers, and everyone else who lent a helping hand along the way.

University of Maryland, College Park
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Food and Drug Administration
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Sponsors of the 2011 MARM

We are very grateful for the contributions that have been provided to the 2011 Middle Atlantic Regional Meeting of the American Chemical Society on the campus of the University of Maryland in College Park. Their generous donations help fuel the energy that allows this volunteer program to take place.

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Rhodium Sponsor

http://www.nist.gov

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http://www.edatatrace.com
Sponsors of Symposia at the 2011 MARM

The support of the following sponsors for specific symposia is gratefully acknowledged. Their contributions aided the symposium organizers in providing funding for speakers and symposium participants who might not otherwise been able to attend.

ChemGenes – for "Damage, Repair and Mutation of DNA" and “Nucleic Acid Chemistry” (Gold Sponsor)

http://www.chemgenes.com

Ocean NanoTech - for “Chemistry of Graphitic Materials” (Silver Sponsor)

http://www.oceannanotech.com
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ACS Division of Chemical Education – for ACS Division of Chemical Education Region Awards for Excellence in High School Teaching (Silver Sponsor)

http://www.divched.org/

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http://www.organicdivision.org

Agilent-Delaware Office – for “Advanced Applications of Separations Sciences”

W. R. Grace – for “Metal-Mediated Small Molecule Activation and Functionalization”

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Exhibitors at MARM 2011

Alfa Aesar, a Johnson Matthey Company, is a leading international manufacturer and supplier of research chemicals, metals and materials. With over 33,000 products listed in its main catalog, Alfa Aesar is the single source for customers' chemical and material needs, from sizes for research to semi-bulk and bulk quantities. The Alfa Aesar Catalog carries organic compounds, high purity inorganics, pure metals, alloys, elements, precious metal compounds and catalysts, rare earths, AA/ICP standards and more. Virtually all products are in stock for immediate shipment.

Bruker is a leading provider of Separation and Mass Spectrometry instruments for the Analytical Sciences. Our innovative and easy-to-use product families (ESI-TOF, Ion Trap, FTMS, MALDI-TOF, LC, GC, GC-MS, ICP-MS) provide the highest performance, highest value systems for a wide range of small molecule, polymer, and biomolecule analysis applications.

In addition to our wide selection of glassware and equipment for chemistry we have begun adding products for chromatography and cell culture keeping us on the forefront of scientific innovation. CGLS fabricates standard glassware items and components as well as custom glassware. We have the capability to produce not only the most complex glass apparatus, but also intricate electronic equipment and customized machined components. Products include process reactors from 10L-100L, benchtop reactors from 100mL-5L. Also on display: Huber Unistat Circulators, Chromatography vials and closures, NMR Tubes, OptiTherm Blocks, Pie-Blocks-Reaction blocks, Pressure Vessels, Volumetric Flasks, Schlenk Glassware/Manifolds, Rotary and Fritted Glassware.
The Council on Undergraduate Research (CUR) and its affiliated colleges, universities, and individuals share a focus on providing undergraduate research opportunities for faculty and students at all institutions serving undergraduate students. CUR believes that faculty members enhance their teaching and contribution to society by remaining active in research and by involving undergraduates in research. CUR’s leadership works with agencies and foundations to enhance research opportunities for faculty and students; provides support for faculty development; develops publications and outreach activities designed to share successful models and strategies for establishing and institutionalizing undergraduate research programs; and provides information on the importance of undergraduate research to state legislatures, private foundations, government agencies, and the U.S. Congress. For more information visit www.cur.org or contact us at cur@cur.org.

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John Wiley & Sons, Inc. is a family-owned, international company that was founded in 1807. Between textbooks, professional titles, and journals, it is the largest publisher of Chemistry titles in the world.
National Organization for the Professional Development of Black Chemists and Chemical Engineers. The NOBCChE Mission is to build an eminent cadre of people of color in science and technology. NOBCChE has developed interactive partnerships over the past three decades with corporate, academic and government entities to generate expanded programs, fellowships and other developmental opportunities to build an eminent, inclusive community of chemists, chemical engineers and other scientists. The limited numbers of African Americans in science-intensive domains have been highly productive. However, severe historic underrepresentation has resulted in a chronic condition of minimal diversity in academic, corporate and government professional talent pools available to develop emerging intellectual constructs and apply creative, practical solutions to local, national and global technical challenges.

If you need to introduce your students to modern electroanalytical chemistry in an easy and inexpensive way, then Pine’s WaveNow potentiostat and Instructional Three-Electrode Cell are exactly what you need! This potentiostat is a lightweight instrument with a USB interface. The instructional cell contains disposable, screen-printed electrodes. www.pineinst.com/echem

As a global leader in analytical X-ray technology, Rigaku is committed to helping solve your small molecule crystallographic problems. Rigaku offers several small molecule crystallography systems—combinations of detector, goniometer, generator, optics, and software—to address your particular needs, including the XtaLAB mini benchtop system for automated three-dimensional structure determination.

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Stop by the Vernier Software & Technology booth to see some of our exciting products for high school and college chemistry. See our powerful computer interface, LabQuest Mini. You can also try out our improved SpectroVis Plus array diode VIS-NIR spectrophotometer, with its improved resolution, wider range (380-950 nm), and fluorometry support. You can also collect data on our popular Vernier Mini GC. The Mini GC is smaller than a shoebox and can use room air as a carrier gas. You can collect, graph, and analyze the data on either a computer or our stand-alone LabQuest lab interface.
GENERAL MEETING INFORMATION FOR MARM 2011

Registration

On-site registration will begin at 8:00 a.m. Saturday, May 21, 2010. Payment can be made by cash, credit card or check. Registration will take place in the room adjacent to the Grand Ballroom in the Stamp Student Center. The registration schedule is:

Saturday May 21: 2010 8:00 AM – 6:00 PM
Sunday May 22: 2010 8:00 AM – 6:00 PM
Monday May 23: 2010 8:00 AM – 6:00 PM

Parking and Shuttle Service

Parking is free in all numbered lots (www.transportation.umd.edu/maps.html). Lot #1 is closest to the Stamp Student Center. Lots # 9 and 11 are closest to the Chemistry Building. Parking is available in Visitor lots, but parking fee is required. A shuttle will operate to and from designated meeting hotels before and after day events on the Maryland campus.

Refreshments at the meeting

Light refreshments will be served during the scheduled morning and afternoon breaks on Saturday and Monday in the Grand Ballroom of the Stamp Student Union (the same room as vendor booths/tables and the poster sessions). Limited lunch venues in the Stamp Student Union will be open on Saturday and Sunday, but we will operate a shuttle to and from College Park restaurants on those days. A list of downtown College Park restaurants within walking distance from the Stamp Student Union will be available at the registration desk.

Mixers

A welcoming reception will be held in the Stamp Student Union from 7:30 – 9:30 PM on Saturday, May 21st. All registrants are welcomed to this free event. On Sunday, May 22nd there will be an ice cream social in the afternoon immediately following the Plenary Addresses at which you will have the opportunity to meet with members of the American Chemical Society’s Board of Directors and the candidates for President-Elect of the American Chemical Society.

Program

Symposia and workshops are listed on subsequent pages. The symposium programs formally begin at 8 AM on Saturday, May 21st, and they continue throughout the three and one half days of the meeting. Look for those that are of interest to you. The Saturday poster session begins at 10:30 AM on Saturday, May 21st, and continues throughout that day, then begins again on Monday, May 23rd, at 8 AM; more than 300 posters were submitted.

Education and Career Activities

Undergraduate and high school education programs are held on Saturday, May 21st. Career symposia and workshops are held on Sunday morning, May 22nd.

Plenary Addresses are Sunday afternoon, May 22nd in Lecture Room 1402 in the Chemistry Building.
MARM 2011 Awards Summary

The ACS Division of Chemical Education Middle Atlantic Region
Award for Excellence in High School Teaching

Mary Catherine Cross, Sherwood High School, Sandy Spring, MD

The E. Emmet Reid Award in Chemistry Teaching at Small Colleges in
the ACS Mid-Atlantic Region

Anita Brandolini, Ramapo College of New Jersey, Mahwah, NJ

The E. Ann Nalley Regional Award for Volunteer Service to the
American Chemical Society

Joan Laredo-Lidell, Fordham University, Bronx, NY

The Chromatography Forum of Delaware Valley – Student Award
Symposium

Donna M. Blackney Beckett, Drexel University
Charles M. Defendorf, Seton Hall University
Paul DeGregory, Drexel University
Justin M. Kontra, Lebanon Valley College
Manasa Mamunooru, Temple University
Adam R. Meier, Bucknell University
Ciara O'Sullivan, Lafayette College
Aravinda C Seneviratne, Bucknell University
The ACS Division of Chemical Education Middle Atlantic Region Award for Excellence in High School Teaching

Dr. Mary Catherine Cross
Sherwood High School
Sandy Spring MD

Mary Catherine Cross received her BA from the University of Tennessee at Chattanooga, her MAT from Teachers College at Columbia University and her PhD in Education Policy from the Catholic University of America. She has taught in the New York City public schools and the District of Columbia public schools in addition to her current assignment at Sherwood High School in nearby Montgomery County, Maryland. Part of her teaching philosophy is to set the tone for student interactions which place the responsibility for learning on the students. She talks about requiring the students to become self-directed learners, constantly assessing what they know, what they need to learn and how they are going to learn it. She provides challenges for the quicker students and support for those who struggle.

Among her creative teaching methods is having her AP Chemistry students create a Chemistry Show after the AP exam in May. The students do twenty to thirty chemical demonstrations. A colleague shared this comment about her:

“The Chemistry Show is typical of Dr. Cross’s philosophy of student learning. In many classes, the teacher is the “star” of the class for chemical demonstrations. In Dr. Cross’s class, the students are the stars and get the applause.”

Dr. Cross has mentored college level students as well and trained graduate students at University of Maryland Baltimore County during the summer. Her exemplary teaching, ongoing student mentoring and exceptional creativity in teaching make her an excellent choice for this year’s High School Teacher Award.
Professor Anita J. Brandolini
School of Theoretical and Applied Science
Ramapo College of New Jersey

Professor Anita J. Brandolini received her BS degree from Drexel University and her MA and PhD degrees from the University of Delaware. She has taught at Rider University, William Paterson University and Fairleigh Dickinson University in addition to her current position at Ramapo College. She is solidly connected to the corporate world through her connection to Jeol USA Inc. She has collaborated with researchers at Jeol and she teaches part of the training program there for their new employees.

She is known for her commitment to excellence in teaching, which goes beyond traditional class and laboratory work to ensuring that her students develop the scientific writing skills and record-keeping standards that will allow for their employability. One of her students said of her:

“While in her class, I found her to be a kind, creative, and sincere educator. I was very impressed by her openness and approachability towards her students. She was always willing to assist in strengthening our weak areas, as well as encouraging our strong ones.”

Her community activities as faculty advisor to the chemistry club, chair of the polymer topical group, councilor for the North Jersey section and the project SEED oversight committee show her to be an engaged and committed exemplar of how to be a 21st century scientist.

She continues to publish both high quality scientific papers and perhaps more importantly book chapters and blog posts which make science more accessible to the community.

Her combination of solid research, exemplary teaching and extensive community outreach contributed strongly to make her this year’s choice for E. Emmet Reid Award.
The E. Ann Nalley Regional Award for Volunteer Service to the American Chemical Society

Joan A. Laredo-Liddell
Fordham University, NY

Joan A. Laredo-Liddell received her BA in Industrial Chemistry and her MA in Chemistry from Hunter College of the City University of New York. She also holds an Advanced Certificate in Educational Supervision and Administration. She has taught at both the High School and College level and this experience informed her capability to engage students and teachers in many, many local section activities.

Joan has been a hard working, dedicated member and volunteer to the New York Section in various capacities. In addition to serving as Chair of the New York Section in 2007, she has served many roles and chaired many committees including National Chemistry Week, CCED Coordinator, Chair of the Westchester Subsection, as well as being a huge advocate for Chemical Education. As a Councilor for the Section she has worked very hard on SOCED to ensure that all students receive the best education possible in the field of Chemistry. She has also contacted local politicians to help them make informed decisions affecting High School Education. This description is only the ‘tip of the iceberg’ to her contributions.

She is admired and respected by her students and her colleagues. The Society and the Section appreciate her hard work and dedication. All of these factors combine to make her an excellent choice for this year’s Nalley Award for Service to the ACS.
The winners will present their work at the DVCF student award symposium on Monday, May 23, from 1:00-5:00 PM. The scheduled presentations are:

**Donna M Blackney Beckett**  Drexel University
Evaluation of Dual-Opposite Injection Capillary Zone Electrophoresis Using a Conventional Capillary Length and Unmodified Cartridge

**Charles M. Defendorf**  Seton Hall University
Using Ferrocene for Improved LC-MS Detection of Arteriosclerotic Chlorinated Fatty Alcohols

**Paul DeGregory**  Drexel University
Enantiomeric separations of cationic and anionic pharmaceutical compounds using dual opposite injection capillary zone electrophoresis with neutral cyclodextrins

**Justin M. Kontra**  Lebanon Valley College
Development of a Project-based Laboratory Involving LC-MS to Introduce Students to Drug Discovery

**Manasa Mamunooru**  Temple University
Capillary and Microfluidic Gradient Elution Isotachophoresis Coupled to Capillary Zone Electrophoresis for Femtomolar Amino Acid Detection Limits

**Adam R. Meier**  Bucknell University
Micellar Electrokinetic Capillary Chromatography investigation of the chiral recognition capabilities of bile salt micelles

**Ciara O'Sullivan**  Lafayette College
Transfer of thin layer chromatography pharmaceutical product screening methods designed for use in developing countries to quantitative High Performance TLC densitometry methods

**Aravinda C Seneviratne**  Bucknell University
Optimizing a short-end electrophoretically mediated micro-analysis (EMMA) assay for creatinine
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<th>Event</th>
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<tr>
<td>On-Site Registration</td>
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<tr>
<td><strong>AM Sessions</strong></td>
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<tr>
<td>Applied Applications of Separation Sciences</td>
<td>8:00 am – 12:00 pm</td>
<td>Margaret Brent B</td>
<td>Huynh-Ba</td>
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<tr>
<td>Synthetic Chemistry across the Border</td>
<td>8:00 am – 12:00 pm</td>
<td>Benjamin Banneker A</td>
<td>Snieckus / DeShong</td>
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<tr>
<td>Medicinal Chemistry and Chemical Biology of Anticancer Agents</td>
<td>8:15 am – 12:00 pm</td>
<td>Benjamin Banneker B</td>
<td>Talisman / Malhotra</td>
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<tr>
<td>New Approaches to Teaching Chemistry I</td>
<td>8:30 am – 12:00 pm</td>
<td>Margaret Brent A</td>
<td>Sinex</td>
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<tr>
<td>Frontiers of Structure and Dynamics using NMR Spectroscopy; Protein Structure and Dynamics</td>
<td>8:30 am – 11:30 pm</td>
<td>Charles Carroll A</td>
<td>Daiye</td>
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<td>Supramolecular Chemistry</td>
<td>8:30 am – 12:30 pm</td>
<td>Charles Carroll B</td>
<td>Davis</td>
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<tr>
<td>Organic Chemistry Poster Session I</td>
<td>10:00 am – 1:30 pm</td>
<td>Grand Ballroom DeShong</td>
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<td>Medicinal Chemistry Poster Session I</td>
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<td>Biochemistry Poster Session I</td>
<td>10:00 am – 1:30 pm</td>
<td>Grand Ballroom DeShong</td>
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<td>Chemical Education Poster Session I</td>
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<tr>
<td>Undergraduate Research Poster Session</td>
<td>10:00 am – 1:30 pm</td>
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<td><strong>PM Sessions</strong></td>
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<tr>
<td>Teachers Award Luncheon</td>
<td>12:00 pm – 1:30 pm</td>
<td>Chemistry Atrium</td>
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<tr>
<td>Advances in Organic Synthesis</td>
<td>1:00 pm – 5:00 pm</td>
<td>Benjamin Banneker A</td>
<td>Wolf</td>
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<td>Event</td>
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<tr>
<td>New Approaches to Teaching Chemistry II</td>
<td>1:00 pm – 4:30 pm</td>
<td>Margaret Brent A</td>
<td>Sinex</td>
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<tr>
<td>Chemistry of Graphitic Materials</td>
<td>1:00 pm – 5:00 pm</td>
<td>Margaret Brent B</td>
<td>Wang</td>
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<tr>
<td>Frontiers of Structure and Dynamics using NMR Spectroscopy</td>
<td>1:00 pm – 5:00 pm</td>
<td>Charles Carroll A</td>
<td>Daiye</td>
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<td>Structure and Dynamics</td>
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<td>Carroll B</td>
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<td>Nanoparticle Metrology</td>
<td>1:00 pm – 5:00 pm</td>
<td>Charles Carroll B</td>
<td>Zachariah</td>
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<tr>
<td>Medicinal Chemistry and Chemical Biology of Anticancer</td>
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<td>Benjamin Banneker B</td>
<td>Talisman / Malhotra</td>
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<td>Agents</td>
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<tr>
<td>Nucleic Acid Chemistry and Biochemistry</td>
<td>1:30 pm – 5:30 pm</td>
<td>Prince George's Room</td>
<td>Rokita / Sintim</td>
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<tr>
<td>Organic Chemistry Poster Session II</td>
<td>2:00 pm – 5:30 pm</td>
<td>Grand Ballroom</td>
<td>DeShong</td>
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<tr>
<td>Medicinal Chemistry Poster Session II</td>
<td>2:00 pm – 5:30 pm</td>
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<tr>
<td>Biochemistry Poster Session II</td>
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<td>DeShong</td>
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<tr>
<td>Chemical Education Poster Session II</td>
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<td>Grand Ballroom</td>
<td>DeShong</td>
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<tr>
<td>Opening Reception</td>
<td>7:30 pm – 9:30 pm</td>
<td>Grand Ballroom</td>
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### Sunday, 22 May 2011

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<tr>
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<tr>
<td><strong>On-Site Registration</strong></td>
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</table>

**AM Sessions**

- **Career Development Workshop** 8:10 am – 12:00 pm, Chemistry Building 1224, Talisman
- **Graduate Research Opportunities in Government Laboratories Workshop** 8:30 am – 12:00 pm, Chemistry Building 1228, Fourkas
- **Environmental Health and Safety Workshop** 9:00 am – 12:00 pm, Chemistry Building 0119, Phifer
- **Building the NSF Grant Proposal Workshop** 9:00 am – 12:00 pm, Chemistry Building 1407, Porter

**PM Sessions**

- **Plenary Lectures of Emerging Problems in the 21st Century** 1:00 pm – 4:00 pm, Chemistry Building 1402, DeShong
- **Ice Cream Social** 4:00 pm – 6:00 pm, Stamp Student Union Atrium

### Monday, 23 May 2011

<table>
<thead>
<tr>
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</table>

**AM Sessions**

- **Food Safety: New Technologies for the Protection of the Food Supply I** 8:30 am – 11:30 am, Benjamin Banneker A, Morehouse / Yakes
- **ACS Career Workshop** 8:00 am – 12:30 pm, Chemistry Building 1407, ACS Careers
- **New Technologies for Lithium Ion Batteries I** 8:30 am – 12:00 am, Charles Carroll A, Kofinas
<table>
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<tr>
<th>Event</th>
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<tr>
<td>Materials Chemistry Poster Session</td>
<td>8:30 am – 12:00 pm</td>
<td>Grand Ballroom</td>
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<td>Inorganic Chemistry Poster Session</td>
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<tr>
<td>Physical Chemistry Poster Session</td>
<td>8:30 am – 12:00 pm</td>
<td>Grand Ballroom</td>
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<tr>
<td>Cheminformatics and Bioinformatics: Working Together to Address Systems Chemical Biology</td>
<td>8:30 am – 12:00 pm</td>
<td>Benjamin Banneker B</td>
<td>Guha</td>
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<tr>
<td>Validation of Chromatographic Methods in Pharmaceutical Chemistry Workshop</td>
<td>9:00 am – 12:00 pm</td>
<td>Chemistry Building 1228</td>
<td>Huynh-Ba</td>
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<tr>
<td>How to Be a More Effective Chemical Hygiene Officer Workshop</td>
<td>9:00 am – 5:00 pm</td>
<td>Chemistry Building 1224</td>
<td>Phifer / Wahl</td>
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<tr>
<td>Science in Start-Up Companies</td>
<td>9:00 am – 12:00 pm</td>
<td>Pyon Su</td>
<td>DeShong</td>
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<td><strong>PM Sessions</strong></td>
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<tr>
<td>Facilitating Improved Lab Scale Purification Workshop</td>
<td>1:00 pm – 5:00 pm</td>
<td>Chemistry Building 1228</td>
<td>Early / Lawrence</td>
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<td>Advances in Terahertz and IR Spectroscopy</td>
<td>1:00 pm – 3:30 pm</td>
<td>Thurgood Marshall</td>
<td>Rahman</td>
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<tr>
<td>Bioactive Small Molecule Design and Discovery</td>
<td>1:00 pm – 4:30 pm</td>
<td>Benjamin Banneker B</td>
<td>Thomas</td>
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<tr>
<td>Redefining the Kilogram and Avogadro’s Number</td>
<td>1:00 pm – 4:00 pm</td>
<td>Chemistry Building 1407</td>
<td>Watters</td>
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<tr>
<td>Expiration of Patent Protection: A Major Challenge Facing the Chemical and Pharmaceutical Industries in the 21st Century</td>
<td>1:00 pm – 4:30 pm</td>
<td>Pyon Su</td>
<td>Hasford / Bianco</td>
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<tr>
<td>Metal-Mediated Small Molecule Activation and Functionalization</td>
<td>1:00 pm – 5:00 pm</td>
<td>Charles Carroll B</td>
<td>Sita</td>
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<td>Analytical Chemistry Poster Session</td>
<td>1:00 pm – 4:30 pm</td>
<td>Grand Ballroom</td>
<td>DeShong</td>
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<td>Chemistry and Materials Composition of Cultural Heritage Materials</td>
<td>1:30 pm – 4:30 pm</td>
<td>Juan Ramon Jiminez</td>
<td>France</td>
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<td>Ambient Ionization Methods for Biological Mass Spectrometry</td>
<td>1:30 pm – 5:00 pm</td>
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<td>CFDV Student Award Symposium for Separation Science</td>
<td>1:30 pm – 4:30 pm</td>
<td>Chemistry Building 1402</td>
<td>Selman</td>
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<td>New Technologies for Lithium Ion Batteries II</td>
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<td>MARM Awards Banquet</td>
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<td>Prince George’s Ballroom</td>
<td>Morehouse / Yakes</td>
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(Ticketed Event)
MARM 2011 WORKSHOPS

Sunday, May 22, 2011

Career Development
Talisman, 8:10 am – 12:00 pm, Chemistry Building 1224

The Career Development Workshop will consist of exciting short talks and panel discussions covering a broad range of topics that include careers in technology transfer, forensics, cosmetic science, genomics, and education. Information on performing job searches, the development of career goals using web based approaches, and strategies for successful networking will be presented.

Graduate Research Opportunities in Government Laboratories
Fourkas, 8:30 am – 12:00 pm, Chemistry Building 1228

The purpose of this workshop will be to expose attendees to the myriad research opportunities present in government laboratories. Also to be discussed will be the options available for funding provided by various government laboratories.

Environmental Health and Safety
Phifer, 9:00 am – 12:00 pm, Chemistry Building 0119

This comprehensive one-day course will identify the various regulatory requirements that apply to laboratories that generate hazardous waste, as well as provide insight into the options for on-site management and off-site disposal. Focus will be on recycling/reclamation techniques, waste minimization, economical handling of wastes, and liability issues. Mr. Phifer has over 30 years experience in managing laboratory wastes for academic and industrial laboratories and is a member and former chair of the ACS Task Force on Laboratory Environmental Health & Safety.

Building the NSF Grant Proposal
Porter, 9:00 am – 12:00 pm, Chemistry Building 1407

Competition for NSF grant awards is especially intense, as increasing numbers of proposals strain the agency’s budget limits. Successful proposals are written by investigators who combine sound principles of grant writing with an understanding of NSF’s overall merit review process. This workshop will focus on critical aspects of interacting with the agency as well as proven techniques for effective writing in each section of the NSF grant proposal. Samples from successful proposals will be cited to illustrate key points.
Monday, May 23, 2011

ACS Career Workshop
ACS Careers, 8:00 am – 12:30 pm, Chemistry Building 1407

Career Workshops will be offered on Planning Your Job Search, Preparing a Resume and Effective Interviewing. These workshops are designed to help chemical professionals and students at all levels understand the current workplace and take advantage of employment opportunities. A Career Consultant will be available to provide individual resume reviews (members must bring a copy of their resume).

How to Be a More Effective Chemical Hygiene Officer
Phifer / Wahl, 9:00 am – 5:00 pm, Chemistry Building 1224

Take a close look at the Chemical Hygiene Officer position, and prepare at the same time for the CHP Certification exam to be held the next day. Phifer and Wahl give a different slant to safety issues in the laboratory, focusing on what you do and how you can do it better. The presenters bring a wide variety of experience to the table, but the real stars of the workshop are you – past attendees note the interactive approach focusing on their problems, from getting administrators involved in safety to dealing with regulatory concerns. The course covers all of the content areas of the certification exam (presented on Sunday through NRCC), including a sample test in the same format as the real one. Whether you are a new Chemical Hygiene Officer or an “old” one, you will find something to put to real use in this fast-paced presentation.

Validation of Chromatographic Methods in Pharmaceutical Chemistry
Huynh-Ba, 9:00 am – 12:00 pm, Chemistry Building 1228

Analytical procedures are used as a quality control tool to monitor the quality and stability of pharmaceutical products. Validation is necessary to confirm the suitability of the analytical method for its intended use. This course will present various validation characteristics from regulatory expectations to practical considerations that apply to chromatographic methods. It will also discuss the key factors to establish validation protocol and acceptance criteria.

Facilitating Improved Lab Scale Purification
Early / Lawrence, 1:00 pm – 5:00 pm, Chemistry Building 1228

This workshop will focus on common issues in lab scale purification with from the perspective of synthetic and isolation chemists. New issues in molecular diversity that require alternate approaches for accelerating a molecules’ progression on to testing, as well as new approaches to improving outcomes for throughput and purity will also be discussed.
“Chemagination” is a contest in which High School students are asked to imagine that they are living 25 years in the future and have been invited to write an article for ChemMatters, a magazine for high school students that focuses on the role of chemistry in everyday life. The subject of the article is: “Describe a recent breakthrough or innovation in chemistry and/or its applications that has improved the quality of people’s lives today.” The article will be written to fit in one of four categories: Alternative Energy Resources, Environmental Concerns, Medicine / Health, or New Materials. In addition to the article, students are asked to design a cover for the magazine. The article must be written as if the student is living in the year 2036, looking back at innovations that have occurred since 2011.

The Regional Chemagination Competition will take place on Saturday, May 21, 2011 at College Park, Maryland. The tentative agenda is as follows:

12:00 pm – 1:30 pm  Set-up and Lunch
1:30 pm – 3:00 pm  Judging
3:00 pm – 4:00 pm  Special Demonstrations and Presentations
4:00 pm – 5:00 pm  Awards and Photos

First place category winners from LOCAL ACS section competitions are eligible to participate. If a first place winner cannot participate for any reason, sections can elect to send an alternate team. If your section did not hold a local competition, interested students could participate directly at the regional level (contact the Chemagination Coordinators for more details).

Contest Coordinators: Kim Morehouse (Kim.Morehouse@fda.hhs.gov) and Louise Lawter (louise.lawter@gmail.com). Event sponsored by the MARM Board.
**PROGRAM**

**Saturday, May 21, 2011 - Morning**

**Synthetic Chemistry across the Border**  
**Metallation Chemistry**  
Stamp Student Union, Benjamin Banneker Room A  
Organizers: P. Deshong, V. Snieckus

8:00 AM  
Introductory Remarks.

8:05 AM  
4. Functionalization of C(sp3)-H Bonds for Synthesis of Complex Molecules. **G. Chen**

8:40 AM  

9:00 AM  
6. Oxidative C-C bond formation mediated by a hypervalent iodine reagent: Developments and applications. **S. Canesi**

9:45 AM  
Intermission.

10:00 AM  
7. 1,2,3-Triazole: Unique ligands in metal coordination and catalysis. **X. M. Shi**

10:35 AM  

10:55 AM  

11:40 AM  
Concluding Remarks.

**Medicinal Chemistry and Chemical Biology of Anticancer Agents**  
Cosponsored by GVK BiO  
Organizers: J. Talisman, S. Malhotra

8:15 AM  
Introductory Remarks.

8:20 AM  

8:50 AM  
11. D-peptide activators of the p53 tumor suppressor for anticancer therapy. C. Zhan, L. Zhao, X. Wu, W. Yuan, M. Pazgier, **W. Lu**

9:20 AM  

9:50 AM  

10:20 AM  
Intermission.

10:30 AM  


12:00 PM Concluding Remarks.

*Chemical Education*

**New Approaches to Teaching Chemistry I**
Stamp Student Union, Margaret Brent Room A
Organizer: S. Sinex

8:30 AM 17. Teaching and learning in the digital age: Chemistry resources teachers and students can rely on from the ChemEd DL. **L. Fanis**, J. W. Moore


10:10 AM Intermission.


11:00 AM 23. Description of a nontraditional freshman-sophomore chemistry sequence and an analysis of student performance. **R. J. Kashmar**


11:25 AM 25. Improving feedback from clicker questions. **D. B. King**

11:45 AM 26. Improving feedback from clicker questions. **D. B. King**

11:50 AM 26. Dissecting the structure-mechanism-reaction paradigm of organic chemistry in a 100-student course with personal response systems (clickers): is 'structure' a threshold concept? **S. M. Graham**

*Frontiers of Structure and Dynamics using NMR Spectroscopy*

**Protein Structure and Dynamics**
Stamp Student Union, Charles Carroll Room A
Organizer: T. Dayie

8:30 AM Introductory Remarks.

8:35 AM 27. Detection of protein conformational Intermediates by NMR relaxation. **R. Ishima**
28. From NMR information to high accuracy biomolecular structures: A quantum chemical pathway. **Y. Zhang**

29. Structural and Dynamics Studies of Microtubule-Associated Proteins by Magic Angle Spinning NMR Spectroscopy. S. Yan, S. Sun, A. Butterworth, S. Ahmed, J. Williams, **T. Polenova**

30. Sensitivity enhancement by nonuniform sampling: theory and applications. **D. Rovnyak**

31. Targeted Xenon-Cryptophane Biosensors for Molecular Imaging. **O. Taratula**, I. J. Dmochowski


33. "Umpolung" molecular containers: Encapsulation of anions and small molecules. **K. T. Holman**

34. Conformational changes in structurally well-defined β-helical peptides on adsorbing to quartz surfaces. **T. D. Clark**, K. P. Fears, J. L. Kulp, D. Y. Petrovykh

35. Self-assembled Nano/microwires of melamine with organic acids -- a new family of proton conductive materials. **H. Ji**

36. Smart assemblies and other adventures in supramolecular space. **J. M. Rivera**

37. Comparison of fibrillar structures and properties of hydro- and organo-gels prepared from (R)-N-alkyl-12-hydroxyoctadecylammonium chlorides, efficient ambidextrous gelators. **V. Mallia**, P. Terech, R. G. Weiss

38. Supramolecular Anion Binders and Transporters. **P. A. Gale**

Concluding Remarks.
Biochemistry Poster Session I
Stamp Student Union, Grand Ballroom
Organizer: P. Deshong

10:00 AM - 1:30 PM

10:00 AM  39. Purification of Amyloid Beta specific antibodies through Surface Plasmon Resonance detection. A. L. Yokom, J. C. Humes, J. M. Finke

10:00 AM  40. Mutagenic effects of Silver Nano particles on bacterial DNA. S. OVANOSIAN, J. Ricciardi, M. Chauhan, M. Tawde

10:00 AM  41. Study of the mechanism of the binding of IHF to the DNA. A. R. Patel, M. Bruist

10:00 AM  42. Enhancement of sensitivity and specificity of carbon nanotubes in diagnosis of prostate cancer based on carbon nanotube field effect transistors Comparison of The Carbon Nano Tube Field Effect Transistor direct binding assay and Enzyme Linked Immunosorbent Assay for detecting Prostate Specific Antigen. S. Chung, K. Ko, S. Chung, M. Kim, S. Stefansson, S. Ahn

10:00 AM  43. Investigation of chemical nature zinc in plants. S. S. Dehipawala, R. Reagon, S. Dehipawala

10:00 AM  44. Structure of Deletion Mutant D5 RNA of a Group II Intron Ribozyme. N. Eldho

10:00 AM  45. Rapid Diagnosis of E. coli using the Carbon Nano Tube Field Effect Transistor Direct Binding Assay. W. Park, S. Chung, M. Kim, S. Ahn

10:00 AM  46. Structure and Function of Selenoprotein K. J. Liu, P. Srinivasan, S. Rosovsky

10:00 AM  47. Ribosomal protein L2: Transmitting information to peptidyltransferase center. S. Musalgaonkar, J. D. Dinman

Chemical Education Poster Session I
Stamp Student Union, Grand Ballroom
Organizer: S. Sinex

10:00 AM - 1:30 PM


10:00 AM  49. The effect of branched alkyl chains on the dynamical properties of ionic liquids. S. Ramati, S. Lall-Ramnarine, M. Gohdo, M. Thomas, J. F. Wishart

10:00 AM  50. Does cold exist? D. W. Solanki

10:00 AM  51. Using Flash movies to envision ionic compound formation. D. W. Solanki

10:00 AM  52. Identifying genes in mycobacteriophages genome. J. Boroday, U. Golebiewska

10:00 AM  53. Using flash technology to assist high school students’ visualization of atmospheric gases. R. Burton

10:00 AM  54. Thermal property of Fe nanoparticles embedded in porous glass medium. M. Sun, S. Dehipawala, T. Cheung
<table>
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<tr>
<th>Time</th>
<th>Number</th>
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<th>Authors</th>
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<tr>
<td>10:00 AM</td>
<td>55.</td>
<td>Co-polymerization of partially sulfonated polyaniline nanofibers for electrostatic interaction with gold nanoparticles.</td>
<td>E. Vanegas, D. M. Sarno</td>
</tr>
<tr>
<td>10:00 AM</td>
<td>56.</td>
<td>Kaltura as a tool for teaching organic chemistry.</td>
<td>J. Tierney, M. Bodek</td>
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<tr>
<td>10:00 AM</td>
<td>57.</td>
<td>An experiment to display the concept of limiting reactants using an iron (III) salicylate complex by utilizing a PASCO colorimeter.</td>
<td>J. Tierney, M. Burch, D. Finneran, H. Roth</td>
</tr>
<tr>
<td>10:00 AM</td>
<td>58.</td>
<td>Examination of mtDNA gene sequence (cytochrome b) to show the evolutionary relationships between regional populations of the brown howler monkey (Alouatta guariba) in the atlantic coastal forest of Brazil.</td>
<td>V. Renard, E. Harris</td>
</tr>
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<td>10:00 AM</td>
<td>59.</td>
<td>Falcon-rodent predation: An introduction to the scientific method.</td>
<td>D. W. Solanki</td>
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<td>10:00 AM</td>
<td>60.</td>
<td>Synthesis of protected oxyallyl silane derivatives for use as homoenolate equivalents.</td>
<td>F. Y. Moslimani, J. A. Pigza</td>
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<tr>
<td>10:00 AM</td>
<td>61.</td>
<td>Development of oxyallyl silanes as homoenolate equivalents in the oxidative addition to substituted phenols.</td>
<td>S. Salarbux, J. A. Pigza</td>
</tr>
<tr>
<td>10:00 AM</td>
<td>62.</td>
<td>Nitration of methyl benzoate -an extension of an old experiment.</td>
<td>D. D. Clarke</td>
</tr>
<tr>
<td>10:00 AM</td>
<td>63.</td>
<td>Gemstone Team ONLINE: How the presence of an audience affects teacher immediacy behaviors in online introductory Chemistry lectures.</td>
<td>M. E. Bowers, B. Paxton, J. Spiegel, L. McLellan, N. Freyman</td>
</tr>
<tr>
<td>10:00 AM</td>
<td>64.</td>
<td>Successful Implementation of Project-Based Biochemistry Laboratory Curriculum at West Chester University of PA.</td>
<td>M. Azam, B. Frost, M. Knabb, L. Rieser-Danner</td>
</tr>
<tr>
<td>10:00 AM</td>
<td>65.</td>
<td>Extraction and analysis of lavender oil from Pennsylvania-grown <em>Lavandula augustifolia</em> for use in fragrances.</td>
<td>H. L. Cronk, T. A. Trumbo</td>
</tr>
<tr>
<td>10:00 AM</td>
<td>66.</td>
<td>Inhibition of thrombin-catalyzed fibrin clot formation by the tetrapeptides LSPR and ISPR.</td>
<td>J. E. North, T. A. Trumbo</td>
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<tr>
<td>10:00 AM</td>
<td>67.</td>
<td>Investigating the chemical interactions between SWNTs and oxides of hafnium.</td>
<td>S. Budhoo, T. Hemraj-Benny</td>
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<tr>
<td>10:00 AM</td>
<td>68.</td>
<td>Formation of porous micron-scale spheres of poly(o-toluidine).</td>
<td>D. LaFaurie, D. M. Sarno</td>
</tr>
<tr>
<td>10:00 AM</td>
<td>69.</td>
<td>Teaching the POGIL way: Perspective of a teaching assistant (TA).</td>
<td>S. Bhattacharya</td>
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**Medicinal Chemistry Poster Session I**

Stamp Student Union, Grand Ballroom
Organizer: P. Deshong

10:00 AM - 1:30 PM

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<tr>
<td>10:00 AM</td>
<td>70.</td>
<td>Nitric oxide-releasing materials for wound healing and surgical applications.</td>
<td>J. A. Hrabie, L. K. Keefer</td>
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<td>10:00 AM</td>
<td>71.</td>
<td>Electrospinning crosslinked chitosan fibers. Part I: Chemical analysis.</td>
<td>C. L. Schauer, M. S. Austero, A. E. Donius, U. G. Wegst</td>
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Novel CXCR4/CCR2 dual-targeted fusion inhibitors. S. McCullough, M. Habib, **X. Wang**


Binding of hydrophobic side chains in the S2’ pocket of Thermolysin: Is it entropic or enthalpic driven binding? **N. Nasief**, B. Adam, G. Klebe, D. Hangauer

Potent anti-cancer activity of heterocyclic compounds with imidazo[4,5-e][1,3]diazepine backbone structure. **M. Xie**, R. S. Hosmane


**Organic Chemistry Poster Session I**
Stamp Student Union, Grand Ballroom
Organizer: P. Deshong


A novel, unusual acid catalysed route to substituted 1,2-dihydropyridine via double decarboxylation. **S. David**

Control of selectivity in the generation and reactions of oxonium ylides. **D. M. Jaber**, R. Burgin, M. P. Doyle

Highly effective one-pot approach to functionalized seven-membered 4,5-dihydrooxepins. **X. Xu**, M. P. Doyle


Photochemical control of CTAB surfactant system through photoisomerization of cinnamic acid derivatives. **R. Heymann**, D. E. Falvey

Oxonium ylide formation and [1,2]-rearrangement to afford an oxybicyclo[4.2.1]nonane. **M. K. Hepler**, M. Doyle, R. Burgin, D. Jaber

Scale-up microwave-assisted synthesis for commercial applications. **R. W. Wagner**, R. Goswami, P. K. Tirunahari, J. H. Brownell

Advances in siloxane-based coupling reactions: Investigation of novel 16-electron palladium(0) tri-olefin catalysts to promote allyl-aryl coupling. **F. E. Nyt-ko, III**, K. Shukla, P. DeShong

Optimization of Dirhodium Caprolactamate Catalyzed Phenolic Oxidations with T-HYDRO. **L. E. Farkas**, M. O. Ratnikov, M. P. Doyle


Synthesis of new highly sensitive light emitting probes for biological and technical applications. **S. Pillai**, L. Wirpsza, S. Marras, Krasnoperov, A. Mustaev

Investigation of Complexes Formed Between Samarium Diiodide and Various Phosphoramides. **C. E. McDonald**

Advances in carbohydrate synthesis: Ionic liquid mediated formation of polyphenolic glycosides. **I. J. Talisman**, V. Kumar, S. V. Malhotra

Free radical scavenging and antioxidant activity of phenolic compounds from onion (*Allium cepa*). **J. S. Sidhu**

Probing of Tetracycline and Zinc Ion interaction. **A. Esa**, R. Desamero


FT-IR spectroscopy characterization of *Bacillus subtilis* sporulation and bacteriophage infection in catabolite rich media. **K. M. Allen**, T. Mysliwiec, D. Aurentz

Context dependence of active-site residues in metabolic enzymes: Knowledge-based tools for enzyme redesign. T. Borbet, T. Fisher, J. Gaston, D. Catt, K. Wang, C. Ricketts, **K. E. Muratore**

Intermediates in the biosynthesis of the antimicrobial phenazine D-alanylgriseoluteic acid. **V. Atanasova**, A. K. Bera, J. F. Parsons

Small Molecule DNA Interaction using Fluorescence Spectroscopy under Different Salt Conditions. **V. Purohit**, m. azam
10:00 AM 105. Synthesis of an electron rich quinone methide precursor to expedite sequence-directed alkylation of DNA. C. Huang, S. E. Rokita

10:00 AM 106. Photodimerization of thymine analogs to simulate the photodimerization implicated in skin cancer. J. Hahn


Undergraduate Research Poster Session
Stamp Student Union, Grand Ballroom
Organizer: P. Deshong

10:00 AM - 1:30 PM

10:00 AM 108. Heterocyclic inhibitors of the helicase of hepatitis C virus. D. L. Bartee, P. J. Smith


10:00 AM 110. Effects of Retinoic Acid on CA-OV3 Ovarian Cancer Cells in Culture. M. P. Kelly, S. L. Miller

10:00 AM 111. Molecular Dynamics of Sarcin-Ricin Domain: Testing of the Variations of a New Force Field. A. M. Johnson, T. Babar

10:00 AM 112. Research work towards a new method of blending powder coatings colors. K. S. Nahan, K. S. Wendling, W. J. Herron

10:00 AM 113. Mechanism of fluorescence quenching of wavelength shifter, BBQ induced by cobalt benzene-1,2-dithiolate. K. Kulick, M. P. Patel, S. A. Varnum

10:00 AM 114. Use of Density functional theory to identify the metal complexes formed by zinc (II) and citrate in aqueous solution. G. Arias De la Rosa, J. Tolentino, R. Z. Desamero

10:00 AM 115. The Role of Retinoic Acid in the Regulation of HOX Genes in Ovarian Cancer Cell Lines. J. A. McGovern, K. S. Wendling, D. R. Soprano

10:00 AM 116. Development of Portable Water Filtering System for Communities in Underdeveloped Countries. S. Lee, S. Chung

10:00 AM 117. Magnetic nanoparticles for drug delivery applications. A. Mugweru, J. Kong

10:00 AM 118. Electrochemical glucose sensor: Redox polymer in β-cyclodextrin inclusion. A. Mugweru, N. Do

10:00 AM 119. Cytochrome c Catalyzes a Reaction Between Ferrous Sulfate and Hydrogen Peroxide. M. Iuliucci, A. Mugweru

10:00 AM 120. Rheology versus structure in hydrotalcites. A. R. Cooper, M. Jitianu

10:00 AM 402. Synthesis and spectroscopic characterization of spiropyran dyes for metal ion detection. K. A. Sennett, S. E. Stitzel

10:00 AM 403. Molecularly imprinted polymers for metal ion detection. M. G. Willen, V. L. Matto, S. E. Stitzel
Saturday, May 21, 2011 - Afternoon

**Advances in Organic Synthesis**

**Synthetic Chemistry**
Stamp Student Union, Benjamin Banneker Room A
Organizer: C. Wolf

1:00 PM  Introductory Remarks.

1:05 PM  121. Adventures in oxidative coupling. **M. Kozlowski**

1:45 PM  122. Cucurbit[n]uril molecular containers. **L. Isaacs**


2:45 PM  124. Optically active 1,1′-spirobiindane-7,7′-diol (SPINOL)-based phosphoric acids as highly enantioselective catalysts for asymmetric organocatalysis. **C. Xing**, Y. Liao, Q. Hu

3:05 PM  Intermission.


4:00 PM  126. Origin of C–H Oxidation Byproducts in Reactions of Glycal Metalla Acyl Nitrenes. **C. M. Rojas**

4:20 PM  127. Microwave-assisted one-pot three component synthesis of isoquinolines by a coupling-annulation sequence. **Y. Chen**


5:00 PM  Concluding Remarks.

**Chemical Education**

**New Approaches to Teaching Chemistry II**
Stamp Student Union, Margaret Brent Room A
Organizer: S. Sinex

1:00 PM  129. Discover the ChemEd DL: Digital resources for the high school chemistry teacher and student. **L. Fanis**, J. W. Moore

1:20 PM  130. “Common Core” standards, student test scores in math computation in the mid-Atlantic states, and the implications for chemistry instruction. **E. Nelson**

1:40 PM  131. Assessing student learning in online general chemistry class. **S. Iyengar**


2:40 PM  Intermission.


3:35 PM  136. Collaborative learning in a private high school second year chemistry class. R. L. Broadrup, B. Hommes

3:55 PM  137. It's in the bag: New approaches to teaching science. D. Valcarcel


*Chemistry of Graphitic Materials*

**Graphene Chemistry**
Stamp Student Union, Margaret Brent Room B
Organizer: Y. Wang


1:30 PM  140. Electrical conductivity of surfactant modified carbon nanotubes. J. Hahn

1:50 PM  141. Ultrahigh concentrations of individually dispersed single-walled carbon nanotube solutions enabled by a co-dispersant. J. D. Leeds, J. T. Fourkas, Y. Wang


2:30 PM  Intermission.


3:50 PM  145. Functionalization of single-walled carbon nanotubes for applications in energy and medicine. M. Ellison, G. Lewis, K. Greco, A. Rimshaw


4:30 PM  147. Simultaneous conductivity and solubility of double-walled carbon nanotubes. A. H. Brozena, J. Moskowitz, B. Shao, S. Deng, H. Liao, K. J. Gaskell, Y. Wang
**Frontiers of Structure and Dynamics using NMR Spectroscopy**

**RNA Structure and Dynamics**
Stamp Student Union, Charles Carroll Room A  
Organizer: T. Dayie

1:00 PM  Introductory Remarks.


2:05 PM  150. Probing the molecular determinants of HIV alternative splicing: NMR and thermodynamic studies of UP1/ESS3. **B. S. Tolbert**, C. Mishler, J. Levengood, P. Rajan

2:45 PM  Intermission.

3:00 PM  151. Optimizing research with NMR instrumentation. **D. M. Baldisseri**

3:30 PM  152. NMR tools for structural biology. **P. A. Keifer**

4:00 PM  153. Translational recoding by a chemo-mechanical retroviral mRNA switch. **V. D’Souza**

4:40 PM  Concluding Remarks.

**Nanoparticle Metrology**
Stamp Student Union, Charles Carroll Room B  
Organizer: M. Zachariah

1:00 PM  Introductory Remarks.

1:05 PM  154. Intelligent design of Nanomaterial for drug delivery: Metrology challenges. **A. K. Patri**

1:45 PM  155. An intuitive yet pragmatic explanation of light scattering by particles. **C. M. Sorensen**


2:25 PM  Intermission.


3:20 PM  158. Elucidating architectures in bimetallic nanostructures. **B. Eichhorn**

3:40 PM  159. Chemical and structural characterization of carbon nanotube surfaces. **K. A. Wepasnick**, H. Fairbrother

4:00 PM  160. On-the-fly measurement of the length distribution and density of nanowires. S. Kim, **G. Mulholland**, M. Zachariah

4:20 PM  Concluding Remarks.
Medicinal Chemistry and Chemical Biology of Anticancer Agents
Stamp Student Union, Benjamin Banneker Room B
Cosponsored by GVK BIO

Organizers: J. Talisman, S. Malhotra

1:10 PM  Introductory Remarks.


2:15 PM  163. NSAID Induction of the p75^{NTR} Tumor Suppressor via the p38 MAPK Signal Transduction Pathway. D. Djakiew

2:45 PM  164. Development of 2,3-disubstituted-1,4-naphthoquinone derivatives as potential therapeutic agents for the treatment for prostate cancer. Y. S. Brandy, S. Berhe, E. Akinboye, I. Ononiwu, D. Adedeji, C. Mouamba, Y. Kanaan, R. L. Copeland, O. Bakare

3:15 PM  Intermission.


3:55 PM  166. Can anti-angiogenic tyrosine kinase inhibitors enhance cancer vaccines? L. A. Emens


4:55 PM  168. Cytotoxicity studies of selected emetine dithiocarbamate ester derivatives in androgen-positive prostate cancer LNCaP cells. E. S. Akinboye, O. Bakare, S. R. Denmeade

5:25 PM  Concluding Remarks.

Nucleic Acid Chemistry and Biochemistry

DNA Bio-organic
Stamp Student Union, Prince Georges Room
Organizers: H. Sintim, S. Rokita

1:30 PM  Introductory Remarks.

1:35 PM  169. Photochemical Regulation of Oligonucleotide Function with Applications to Biological Systems. A. Deiters

Consequences of positively charged thiophosphate protecting groups on the cellular uptake of thermolytic oligonucleotide prodrugs. H. V. Jain, K. Takeda, C. Tami, D. Verthelyi, S. Beaucage


Intermission.


Psoralen photochemistry illuminates cellular pathways of DNA interstrand crosslink repair. M. A. Bellani, M. Paramasivam, J. Huang, D. Fox, W. Wang, A. Smogorzewska, M. M. Seidman


Concluding Remarks.

Biochemistry Poster Session II
Stamp Student Union, Grand Ballroom
Organizer: P. Deshong

Expression and purification of the protease and the receptor binding domains of Botulinum neurotoxin A. M. Feng, D. C. Yang

Insertion of selenocysteine into the redox-active cysteine-x-x-cysteine motif of the flavoprotein augmenter of liver regeneration. S. A. Schaefer, R. Rubenstein, C. Thorpe, S. Rozovsky

Turnip Mosaic Virus Genome-Linked Protein (VPg) Inhibits Pokeweed Antiviral Protein (PAP)-Mediated Depurination of RNA. A. V. Domashevskiy, K. Noro, D. E. Friedland, D. J. Goss

To develop alternative therapeutic approaches to the treatment of opportunistic infections. A. Agarwal, D. B. Hansen

Testing the biochemical mechanism for the activation of apoptosis by the mitochondrial enzyme cytochrome c heme lyase (CCHL). L. Fredericks, T. Weller, C. Sanders, M. Junker

Regulating multimeric enzymes by engineering controllable self-associating inhibitor proteins. J. Sabatine, R. Wagner, C. Young, M. Junker

Elasticity of Intrinsically Disordered Nebulin Modules. J. G. Forbes, R. J. Wittebort, A. Grishaev, W. L. Tsai, K. Wang

Measuring of the release of DNA subsites from the DNA-IHF complex. P. J. Bhatiya

Using the Funcational Amino Acid Navigator to Understand Differences Between Substrate and Allosteric Efferctor Binding. J. Cargill, S. Gomez, R. Solimeo, P. Palenchar
2:00 PM 185. $^{77}\text{Se}$ as a Probe of Methionine’s Role in Protein-Protein and Protein-Ligand Interactions. **Y. Pepelyayeva**, S. Rozovsky

2:00 PM 186. Maximum incorporation of selenium in *E. Coli* cells for NMR spectroscopy. **R. Rubenstein**, W. Wilkie, Y. Pepelyayeva, S. Rosovsky

2:00 PM 187. $^{77}\text{Se}$ NMR spectroscopy of selenoproteins’ redox motifs. **F. Li**, S. Rozovsky

*Chemical Education Poster Session II*

Stamp Student Union, Grand Ballroom
Organizer: P. Deshong

2:00 PM - 5:30 PM

2:00 PM 209. Using the Folin-Ciocalteau Method to measure the total amount of antioxidants in tea samples and other beverages. **M. M. Moe**, S. Svoronos, P. Irigoyen, P. Svoronos

2:00 PM 204. Determination of gallic acid in teas and other beverages using high pressure liquid chromatography. **B. Kane**, S. Svoronos, P. Irigoyen, P. Svoronos

2:00 PM 203. The technology of biosolids as applied to wastewater at New York City’s Division of Environmental Protection. **K. Chavez**, W. Kelly, F. Jacques, P. Meleties, P. Svoronos

2:00 PM 202. Recycling wastewater at New York City’s Division of Environmental Protection: An ATE grant summer internship. **M. Morales**, W. Kelly, F. Jacques, P. Meleties, P. Svoronos

2:00 PM 201. Application of microbiology at the wastewater treatment plant of the New York City Environmental Protection (DEP). **M. M. Moe**, F. Jacques, W. Kelly, P. Meleties, P. Svoronos

2:00 PM 200. Determination of the ionization constant of carboxylic acids using microscale freezing point determination measurements. **F. Nazumudeen**, P. Irigoyen, P. Svoronos

2:00 PM 199. Reactivity of tris (trimethylsilyl) phosphite (TMSP): Synthesis of the bisphosphonic acid of phenylalanine. **K. Chavez**, M. Morales, L. Vargas

2:00 PM 198. Reactivity of tris (trimethylsilyl) phosphite (TMSP): N-mustard-bisphosphonic acid of bicine. **M. Morales**, K. Chavez, L. Vargas

2:00 PM 197. Pathways to chemical technology education and careers: A student internship analyzing water quality. **X. Ye**, P. Svoronos, P. Meleties, B. Ranheim, N. Yao

2:00 PM 196. A DSSP model of interaction between modified Poria cocos D-glucan and murine DECTIN1 receptor. **E. Ahn**, T. Cheung

2:00 PM 195. Calculation of the degree of ionization of salts in aqueous solutions as a function of concentration using microscale freezing point determination measurements. **M. Balducci**, P. Irigoyen, P. Svoronos

2:00 PM  207. Concentration dependence of refractive index measured by a laser pointer: Refractive index vs. concentration. R. Cho, E. Yang, J. H. Shin

2:00 PM  206. Determination of copper content of the US penny by visible spectroscopy and x-ray fluorescence. S. Jagdeo, R. Burgjia, J. H. Shin

2:00 PM  205. Determination of copper content of the US penny by x-ray fluorescence and gravimetric method. R. Burgjia, S. Jagdeo, J. Shin

2:00 PM  194. Catalytic, solvent-free preparation of N-(2-(pyridin-2-yl)-ethyl)sulfonamides. P. Ghattas, D. L. Jacobs

2:00 PM  193. Glycolate alkylations with 2-(methyliodo)acrylates toward the synthesis of majorynolide & majorenolide. L. E. Musumeci, D. L. Jacobs

2:00 PM  192. Heavy metals in everyday items by x-ray fluorescence (xrf) spectrophotometry. W. Guneid, J. Iorio, B. Montalbano, I. Runtenburg, A. Smithson, T. Xu

2:00 PM  191. Heavy metals in golf balls and fishing lures by x-ray fluorescence (xrf) spectrophotometry. A. Smithson, J. Iorio, B. Montalbano, I. Runtenburg, T. Xu

2:00 PM  190. Theoretical calculations of the adsorption of lysine on montmorillonite surfaces. A. Chugh, L. Tribe

2:00 PM  189. 5-aminovaleric acid adsorption to montmorillonite surfaces: Theoretical calculations. P. Balliet, M. Zekarias, L. Tribe

2:00 PM  188. A Proposed Method to Ascertain Racial Differences in Hair Structure Using Proteomics. I. Shomer

Medicinal Chemistry Poster Session II
Stamp Student Union, Grand Ballroom
Organizer: P. Deshong

2:00 PM - 5:30 PM


2:00 PM  213. Flexible docking in tandem with linear discriminant analysis as a tool to generate hypotheses on the binding of agonists and blockers to G protein-coupled receptors. S. Costanzi, J. Karpiak, B. Berk, S. Vilar

2:00 PM  214. Design, synthesis, and evaluation of 2,3-Diphosphoglycerate analogs as stabilizer and affinity modulator of hemoglobin. T. W. Kassa, J. S. Matthews

2:00 PM  215. Protein polymer conjugates and curcumin conjugates for biomedical applications. K. S. Raja, S. Dolai, W. Lamrouex, P. Banerjee
| 2:00 PM | 216. Hydroxy-pyrrolopyridine-trione Based HIV-1 Integrase Inhibitors | X. Zhao, K. Maddali, S. J. Smith, M. Mathieu, B. Johnson, B. Vu, C. Marchand, S. Hare, P. Cherepanov, S. H. Hughes, Y. Pommier, T. R. Burke, Jr. |
| 2:00 PM | 217. Elucidation of the reaction between aryl-boronic acids and cis-diols | J. W. Tomsho, S. J. Benkovic |
| 2:00 PM | 220. Halogenated enaminoes as potential anticonvulsant agents | I. Edafiogho, K. Ananthalakshmi, M. Qaddoumi, O. Phillips, S. Kombian |
| 2:00 PM | 221. Peptide-capped Gold Nanoparticles: Design, Characterization, and Their Application in Drug Delivery | A. Nasrolahi Shirazi, D. Mandal, R. Tiwari, K. Parang |
| 2:00 PM | 222. Presence in human CYP1A2 gene of -163C>A SNP insufficient for predicting perceived caffeine sensitivity | C. J. Park |
| 2:00 PM | 223. Expression and Purification of Mycobacterium tuberculosis Sigma Factor (SigA) for in vitro transcription assays | C. J. Holt, S. K. Gill, G. A. Garcia |
| 2:00 PM | 224. Discovery of Novel Macrolide Antibiotics | B. S. Wagh, T. Paul, V. Velvadapu, I. Glassford, R. B. Andarde |
| 2:00 PM | 225. Receptor specific vasopressin antagonists | N. Heindel, C. Guillon, K. Fabio, S. Lu, M. Brownstein, E. Damiano, C. Garippa, E. Coccaro, C. Ferris, M. Miller, G. Koppel, M. Steiner, N. Simon |
| 2:00 PM | 226. Broad Spectrum Anticancer Activity of 5:7:5-Fused Diimidazodiazepine Analogues | A. Kondaskar, S. Kondaskar, R. Hosmane, J. Fishbein |

**Organic Chemistry Poster Session II**
Stamp Student Union, Grand Ballroom
Organizer: P. Deshong

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<th>2:00 PM - 5:30 PM</th>
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2:00 PM 231. Cationic chiral dirhodium carboxamidates as Lewis acid catalysts. X. Wang, M. P. Doyle
2:00 PM 232. Synthesis and applications of functionalized diazoacetacetates. Y. Liu, M. P. Doyle
2:00 PM 233. Amine heterocycle synthesis via rhodium(I)-catalyzed intramolecular hydroac-
ylation. H. D. Bendorf
2:00 PM 234. Blue bottle reaction: Revised. P. Murthy, K. Rizzolo
2:00 PM 235. Versatility of calixarene reactions with 1,3-dibromopropane. S. T. Hailu, P. F. Hudrlik, A. M. Hudrlik, R. J. Butcher
2:00 PM 236. Synthesis and study of capped and tetrachelate/dichelate porphyrin chromo-
phores on metal oxide semiconductor surfaces. K. Chitre, S. Coh, S. Rangan, R. Bartynski, E. Galoppini
2:00 PM 237. Functionalized catanionic surfactant vesicles for drug delivery and vaccine ap-
plications. L. H. Stocker, A. Horn, R. Richards, P. DeShong
2:00 PM 238. Cyclopropyl Aziridines: Solvolytic Reactions of the Tosyl Aziridine of (+)-2-Carene. J. M. Rabb, L. J. Silverberg
2:00 PM 239. Novel ring expansion of a vinyl cyclopropane to a vinyl azetidine via a cyclopro-
pyl bromonium ion. K. A. Brobst, L. J. Silverberg
2:00 PM 240. Membrane anion transport of alkylamido Ceramide analogues. S. Bahmanjah, N. Zhang, J. Park, J. T. Davis
2:00 PM 241. Amino acid derivatives as ion transporters. S. Rastogi, G. M. Peters, A. J. Olsen, J. T. Davis
2:00 PM 242. Electrochemical Studies of Ketone : Lewis Acid Interactions. G. T. Cheek
2:00 PM 243. Improved process for the preparation of PhINTs. N. M. Celani, L. J. Silverberg
2:00 PM 244. New HNO precursors based on bis-acylated hydroxylamines, N-acyloxysulfon-
amides, and N-hydroxy-N-acylsulfonamides. A. D. Sutton, J. P. Toscano
2:00 PM 245. Synthesis of quaternary centers mediated by a hypervalent iodine reagent and its application to total synthesis. K. Guerard, C. Sabot, M. Beaulieu, S. Canesi
2:00 PM 246. Stereoselective synthesis of substituted cis-hydrindanes. J. Liu, M. A. Marsini, E. J. Sorensen
2:00 PM 247. Self-assembly of small organic molecules in aqueous solutions. D. Subraman-
nian, M. Anisimov
2:00 PM 249. Bisphosphonamidate clodronate prodrug exhibits potent anticancer activity in A549 NSCLC cells. M. R. Webster, C. L. Hann, C. L. Freel-Meyers
2:00 PM 249. Bisphosphonamidate clodronate prodrug exhibits potent anticancer activity in A549 NSCLC cells. M. R. Webster, C. L. Hann, C. L. Freel-Meyers
2:00 PM 250. 1-Deoxy-D-xylulose 5-phosphate synthase: A new twist in thiamine diphosphate-
dependent enzymology. L. A. Brammer, J. M. Smith, H. Wade, C. F. Meyers
2:00 PM  251. Reversibility of HNO-induced sulfinamide formation. **G. Keceli**, J. P. Toscano
2:00 PM  252. Inhibition of *Francisella novicida* growth in Conditioned Media: Biosignaling mechanism. **G. S. Karman**, M. W. Durham-Colleran, M. L. van Hoek
2:00 PM  253. DXP synthase-catalyzed C-N bond formation: Implications for inhibitor design. **C. Freel Meyers**, F. Morris
2:00 PM  255. Thioamides as fluorescence quenchers: Minimalist chromophores to monitor protein dynamics. **J. M. Goldberg**, S. Batjargal, A. M. Klein, E. Petersson
2:00 PM  256. Design and synthesis of novel hemoglobin crosslinkers based on 2,3 Diphosphoglycerate. **C. Cunningham**, T. Kassa, J. Matthews
2:00 PM  257. Recognition and alkylation of DNA by PNA-QMP conjugates. **Y. Liu**, S. E. Rokita
2:00 PM  258. Criteria for Increasing Efficiency of Excess Electron Transfer in DNA. **A. Fakhari M.**, Y. K. Chen, S. E. Rokita

**Sunday, May 22, 2011 - Morning**

**Career Development Workshop**
Chemistry Building, 1224
Organizer: J. Talisman

8:10 AM  Introductory Remarks.
8:15 AM  259. A career in chemistry—a personal journey. **W. F. Koch**
8:35 AM  260. Innovative, low cost and replicable strategies to help students develop their career goals using web-based technologies. **R. Khan**
9:15 AM  262. Beyond the bench. **L. A. McDonald**
9:35 AM  Intermission.
9:45 AM  263. Networking you way to your next position. **W. H. Suits**
10:05 AM  264. Careers in forensic chemistry: What they don’t tell you on CSI. **J. E. Schaff**
10:25 AM  265. Careers in Technology Transfer and Business Development. **S. M. Ferguson**
10:45 AM  Panel Discussion.
11:20 AM  Panel Discussion.
Graduate Research Opportunities in Government Laboratories
Chemistry Building, 1228
Organizer: J. Fourkas

8:30 AM 266. Working with the National Institute of Standards and Technology: Research Collaborations, Funding, and Facilities Use. D. Poster


9:10 AM 268. Raman spectroscopy for biodiesel determination. R. A. Richards

9:30 AM 269. Partnership for Cancer Technology between the University of Maryland and the National Cancer Institute. W. Losert

Building the NSF Grant Proposal
Grant Writing Workshop
Chemistry Building, 1407
Organizer: R. Porter

Sunday, May 22, 2011 - Afternoon
Emerging Problems in the 21st Century
Chemistry Building, 1402
Organizer: P. Deshong

1:00 PM Introductory Remarks.
1:05 PM 270. Current status in understanding climate and climate change prediction. J. E. Penner
1:45 PM 271. The re-emergence of infectious diseases. C. E. Barry
2:25 PM Intermission.
3:15 PM Concluding Remarks.

Monday, May 23, 2011 - Morning
Advances in Terahertz and IR Spectroscopy
Terahertz Spectroscopy
Stamp Student Union, Thurgood Marshall Room
Organizer: A. Rahman

8:30 AM Introductory Remarks.
8:35 AM 431. Terahertz spectrometric characterization of organic and biological compounds in aqueous solution. T. L. Broadt, A. Rahman
9:05 AM 432. Structural characterization of amino-terminated organic thin films on solid substrates by infrared-visible sum frequency generation vibrational spectroscopy and other complimentary surface analytical techniques. J. Kim, G. J. Holinga, G. A. Somorjai


10:05 AM

Intermission.


11:10 AM 438. Quantitation of gaseous pollutants at ppm concentrations using THz-TDS. R. Smith, M. A. Arnold

11:30 AM 439. USP spectroscopic identification tests. J. M. Smeller

11:50 AM

Concluding Remarks.

Cheminformatics and Bioinformatics: Working Together to Address Systems Chemical Biology

Chemical Genomics
Stamp Student Union, Benjamin Banneker Room B
Organizer: R. Guha

8:30 AM

Introductory Remarks.

8:35 AM 273. Analyzing protein-protein interactions for annotation prediction. C. Kingsford

9:00 AM 274. Merging biological and chemical spaces using machine learning approaches. H. Rangwala

9:25 AM 275. FDA/USP Substance Registration System (SRS) as an informational bridge between chemistry and biology. F. L. Switzer, L. N. Callahan, T. A. Peryea

9:50 AM 276. Cross validation of the biomedical data from disparate chemogenomics databases: Application to the serotonin receptor 5-HT1A ligands. X. Wang

10:15 AM

Intermission.

10:25 AM 277. Role of C Terminus of Bacteriorhodopsin in protein stability. F. Rezae, S. Kelty


11:15 AM 279. Identification and Visualization of Specificity-Determining Residues Via Multi Subgroups Covariation Analysis. S. n. Sheftel, K. n. Muratore
## Food Safety: New Technologies for the Protection of the Food Supply I

### Food Safety
Stamp Student Union, Benjamin Banneker Room A
Organizers: K. Morehouse, B. Yakes

<table>
<thead>
<tr>
<th>Time</th>
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<tr>
<td>8:30 AM</td>
<td>Introductory Remarks.</td>
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<td>8:40 AM</td>
<td>280. Food safety modernization act: overview of the new law and impact on laboratories. <strong>S. M. Cole</strong></td>
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<td>9:10 AM</td>
<td>281. FDA/USP Substance Registration System (SRS) as a tool for codifying food ingredients. <strong>F. L. Switzer, L. N. Callahan, H. S. Crandall</strong></td>
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<td>9:50 AM</td>
<td>283. QuEChERS sample preparation: Advancements and modifications in the methodology. <strong>J. Stevens, L. Zhao, A. Zhai</strong></td>
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<td>10:10 AM</td>
<td>Intermission.</td>
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<td>10:30 AM</td>
<td>284. LC-MS/MS detection of glycidyl esters and 3-MCPD esters in edible oils. <strong>S. Mahon, T. H. Begley, G. W. Diachenko</strong></td>
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<td>10:50 AM</td>
<td>285. Determination of siloxanes in silicone nipples and potential migration to milk/formula products. <strong>K. Zhang, J. W. Wong, T. Begley</strong></td>
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<td>11:10 AM</td>
<td>286. Development of an isotope dilution assay for the regulatory analysis of the allergenic milk protein α-S1-casein utilizing an intact 15N-labeled protein internal standard. <strong>P. F. Scholl, G. A. Newsome, J. Callahan</strong></td>
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<td>11:50 AM</td>
<td>Concluding Remarks.</td>
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### Inorganic Chemistry Poster Session
Stamp Student Union, Grand Ballroom

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<tr>
<td>8:30 AM</td>
<td>289. Expanding the Range of Polyolefins through Living Coordinative Chain Transfer Polymerization. <strong>J. Wei, W. Zhang, R. Wickham, L. Sita</strong></td>
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<td>8:30 AM</td>
<td>290. Effects of Strong Donor/Acceptor Electronic Mixing in Ruthenium(II) poly-pyridyl Complexes Manifested in their Spectroscopic and Electrochemical Properties and Supported by Computational Methods. <strong>M. M. Allard, J. F. Endicott</strong></td>
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<td>8:30 AM</td>
<td>291. Hydrogenation of Quinoline by Palladium nanoparticles on MgO. <strong>R. Rahi, R. A. Sanchez-Delgado</strong></td>
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8:30 AM 292. Precision Polymers from Living Coordinative Chain Transfer Co- and Terpolymerization of Ethene, Norbornene and α-Olefins. R. R. Wickham, L. R. Sita

8:30 AM 293. Synthesis, electrochemical and computational studies of (η⁴-C₅Ph₄=O)Fe(CO)₂L. B. A. Povirk, E. S. Donovan, G. A. Felton

8:30 AM 294. Design aspects of organometallic electrocatalysts for hydrogen production. S. E. Froberg, E. S. Donovan, G. A. Felton


8:30 AM 296. Synthesis of ferrocenyl alcohols as precursors to acrylate and methacrylate monomers. S. Lovelace-Cameron, B. Humphrey, D. Formby, J. Rutledge

8:30 AM 297. The facile fabrication of PtSn₄ and Ir₃Sn₃ intermetallic nanoparticles from bimetallic Zintl clusters. D. O. Downing, Z. Liu, B. W. Eichhorn

8:30 AM 298. Use of di(p-hydroxybenzylidene)acetone palladium(0) compounds in the synthesis of organopalladium complexes. B. A. Harding, C. Callmann, F. E. Goodson

8:30 AM 299. Design and synthesis of chelating chiral phosphine compounds as potential ligands for catalysis. S. E. Ingram, M. J. Bertocchi, C. Supplee

8:30 AM 300. Synthesis, characterization, and anticancer effects of a 4-hydroxy pyridine derivative of NAMI-A. T. Zhou, K. J. Humphreys

8:30 AM 301. Synthesis of Low-Coordinate Manganese Clusters. C. Lam, M. J. Zdilla

8:30 AM 302. Ruthenium nanoparticles supported on Poly(4-vinylpyrididine) as catalyst for hydrogenation of aromatics and evidence for a dual site mechanism. M. Fang, R. A. Sánchez-Delgado

8:30 AM 303. Small Molecule Activation by Group 6 M(IV) Terminal Oxo and Imido Complexes Supported by the Monocyclopentadienyl, Amidinate Ligand Set. B. L. Yonke, W. Farrell, J. Reeds, P. P. Fontaine, P. Y. Zavalij, L. R. Sita

8:30 AM 304. Ruthenium catalyzed hydrogenation supported by a novel bipyridyl ligand. I. Nieto, M. S. Livings, M. Zeller, E. T. Papish

8:30 AM 305. Determination of iron in vitamin pills by a redox titration and spectrophotometry technique. Y. A. Akaragwe, G. M. Lekane


8:30 AM 307. Comparison of the reactivities of a terminal alkene and an internal alkyne in platinum-catalyzed hydrosilylation reactions. M. K. Kolel-Veetil, T. M. Keller

8:30 AM 308. Organoaluminum effect on stereoselection in heterocyclic amines. J. Hahn

8:30 AM 309. Synthesis and characterization of Zn bis β-difunctional complexes for the fabrication of ZnO via metal organic chemical vapor deposition for applications in Microelectronics. K. Johnson, B. Zhang, H. Katz, J. Matthews
8:30 AM 310. New Au(III), Pt(II) and Pd(II) complexes with water soluble iminophosphorane ligands as potential anticancer drugs. **M. Carreira, M. Contel**

8:30 AM 311. Luminescent di and trinuclear organometallic gold(I)-M (Au₂, Au₂Ag and Au₂Cu) compounds containing bidentante phosphanes as active antimicrobial agents. **M. Frik, J. Jiménez, I. Gracia, L. Falvello, S. Abi-Habib, K. Suriel, T. Muth, M. Contel**

8:30 AM 312. Titanocene-phosphine derivatives as precursors to cytotoxic heterometallic TiAu₂ and TiM (M = Pd, Pt) compounds. **J. Gonzalez-Pantoja, M. Stern, A. Jarzécki, E. Royo, A. Varela, R. J. Aguilera, M. Contel**

**Materials Chemistry Poster Session**
Stamp Student Union, Grand Ballroom
Organizer: P. Deshong

8:30 AM - 12:00 AM

8:30 AM 313. Structural effects of de-alloying the less noble metal from silver-gold thin films. **D. A. McCurry, M. Kamundi, M. Fayette, F. Wafula, N. Dimitrov**

8:30 AM 314. Resilin in the engineering of elastomeric biomaterials. **L. Li, K. L. Kiick**


8:30 AM 316. Uranyl-4,4′-biphenyldicarboxylates: Synthesis, Structure and Fluorescent Properties. **P. Cantos, C. Cahill**


8:30 AM 318. Synthesis and characterization of a novel uranyl thiophene coordination polymer. **S. G. Thangavelu, C. L. Cahill**


8:30 AM 320. Fabrication and characterization of electrospun semiconductor nanoparticle – polyelectrolyte ultra-fine fiber composites. **J. S. Atchison, C. L. Schauer**

8:30 AM 321. Post-processing electrospun chitosan fibers. **M. S. Austero, A. C. Toth, C. L. Schauer**

8:30 AM 322. Effects of changing reaction parameters on Suzuki polycondensations. **P. R. Melvin, F. E. Goodson, A. G. Bal, E. A. Davey, B. A. Harding**


8:30 AM 324. Trifluoro ethanol and ¹⁹F MAS NMR as a terminal hydroxyl probe for zirconium(IV) hydroxide structures. **J. B. DeCoste, G. W. Wagner, G. Mogilevsky, G. W. Peterson**

8:30 AM 325. Preparation and modeling of CuO nanoparticles formation and growth in flame spray pyrolysis. **C. Chiang, K. Aroh, S. Ehrman**

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328. Fabrication and characterization of UV-emitting defect-free ZnO nanoparticles. D. Micheroni, T. S. Ahmadi, A. Turner, E. Ruaneh

329. Electrical properties of a rod-shaped virus. L. M. Parsons, S. Kramer, J. Culver

330. Functionalized metal oxide surfaces for electrocatalytic applications. K. N. Crowder, S. Almahdali, B. Wenberg

331. Fabrication and characterization of CdTe nano- and microstructures for photo-electrochemical solar cells application. M. Osial, J. Widera, K. Jackowska

332. Structures of brominated oligothiophenes and ethylenedioxythiophenes: Combined experimental and theoretical studies. P. T. Pham

333. Photo-Induced Oxidation of Arsenite to Arsenate on Ferrihydrite. N. Bhandari, R. J. Reeder, D. R. Strongin

334. Studies of phase formation of Zn_{1-x}M_{x}TiO_{3} (M= Mg or Mn, x < 0 < 0.5) from various wet chemical methods. C. DelGrosso, C. Ely, F. Chen


337. Fluoro-modified melting gels; new materials for hermetic barriers. D. Abogye, A. Jitianu

338. Structural properties of oxide system derived from sol-gel synthesized Ni-Al layered double hydroxides. M. Jitianu, M. Zaharescu, S. Birjega, A. Jitianu

339. One-step synthesis of stable fluorescent porous silica nanoparticles. Q. Liu, M. Zachariah


341. Application of helium pycnometry for determining integrity of coatings on porous substrates. E. D. Seymour, S. L. Conway


343. Toward covalent attachment of proteins to solid surfaces. C. Sun, C. Sha, P. J. Loll, L. S. Penn
8:30 AM 344. Temperature dependent excimer and exciplex fluorescence of pyrene-containing molecules as probes to investigate the micro-structural features of poly(alkyl methacrylate)s. S. -. Abraham, R. G. Weiss

8:30 AM 345. Electrical characterization of highly-conformal carbon films prepared by CVD. H. A. Ali, O. Rabin


8:30 AM 212. Towards the synthesis of novel CK1 inhibitors: An approach using a metal halogen exchange on 2-bormopyridines. V. Paradis

New Technologies for Lithium Ion Batteries I

Polymer Chemistry
Stamp Student Union, Charles Carroll Room A
Organizer, Presiding: P. Kofinas

8:30 AM  Introductory Remarks.

8:35 AM 347. Interfacing Electrolytes with Electrodes in Li Ion Batteries. K. Xu


10:05 AM  Intermission.

10:20 AM 349. Study of high temperature power and capacity fade of Li-ion batteries with LTO anode. Y. Chen

11:00 AM 350. Tin/carbon composite anodes for long cycle life lithium-ion batteries. Y. Xu, C. Wang

Physical Chemistry Poster Session

Stamp Student Union, Grand Ballroom
Organizer: P. Deshong

8:30 AM - 12:00 PM

8:30 AM 351. Water-to-O\textsubscript{2}\textsuperscript{-} binding motifs of O\textsubscript{2}\textsuperscript{-}(H\textsubscript{2}O) and their controlling factors. W. Sheu, M. Chiou

8:30 AM 352. Effects of SDS, CTAB, Triton X-100 and the binary mixtures of Triton X-100/SDS and Triton X-100/CTAB on the electron transfer reaction between tris-2, 2′-bipyridyl iron(II) and azidopentacyanocobaltate(III) complexes. O. A. Oyetunji, G. O. Ogunlusi, J. W. Ige, O. O. Owoyomi

8:30 AM 353. Coherent anti-Stoke Raman scattering (CARS) microscopy of central nervous system (CNS). Y. Kim, J. T. Mason


8:30 AM 355. Synthesis and Electrochemical Studies of ruthenium (Ru) complexes containing multiple metal centers. R. J. Fealy
8:30 AM 356. Application of an electrochemical method that can be used to probe the distal residues in heme proteins to elucidate their roles in oxygen binding and reduction. J. F. Cerda, C. Guzman, E. Amendola, C. Cicco, A. Fritz

8:30 AM 357. Characterizing the protein environmental effects on the reduction potential. B. S. Perrin, T. Ichiye

8:30 AM 358. Molecular dynamic simulation of dicarboxylic acid coated aqueous aerosol: structure and processing of water vapor. X. Ma, P. Chakraborty, B. Henz, M. Zachariah

8:30 AM 359. Re-deposition of oxidants on icy outer solar system bodies. N. Do, P. Cooper


8:30 AM 363. Reaction of OH and CH₃ Radicals by Laser Photolysis- Transient Absorption over the 0.01-100 Bar Pressure and 295-714 K Temperature Ranges. M. Sangwan, E. N. CHESNOKOV, L. N. KRASNOPEROV

8:30 AM 364. Reaction of methylenehydrazine with singlet oxygen (¹O₂). &. Castillo, A. Ghogare, A. Greer


8:30 AM 366. Torsion potential for hydroxylamine. R. C. Mayrhofer

8:30 AM 367. Quantum calculations on (H2O)x.HO complexes. D. Voglozin, P. Cooper

8:30 AM 368. Quantization of the Gibbs free energy levels of enzymes in living cells: Experimental evidence. S. Ji

8:30 AM 369. Chiral supramolecular structures for the detection of chemical changes in aqueous environment. P. V. Shibayev, C. Schlesier, S. McDonald


8:30 AM 371. New method for aerosol measurement of particle density and porosity. Q. Liu, M. Zachariah

Science at Start-Up Companies
Stamp Student Union, Pyon Su Room
Organizer: P. Deshong
Monday, May 23, 2011 - Afternoon

**Applied Applications of Separation Sciences**

*Chromatography*

Stamp Student Union, Thurgood Marshall Room

1:00 PM  Introductory Remarks.

1:05 PM   1.  GCxGC-ToFMS: A Chromatography Sandbox. **N. H. Snow**

1:35 PM   3.  Chromatographic applications and beyond in the Agricultural Industry. **M. P. McNally**

2:05 PM   Fast and Faster - Conversion of HPLC Methods to VHPLC methods.

2:35 PM   High Throughput Drug Analysis in LC/MS.

3:05 PM   2.  Electrostatic Interactions and the Implications on Peak Tailing of Bases. **B. Biddlingmeyer**

3:35 PM   Concluding Remarks.

**Analytical Chemistry Poster Session**

Stamp Student Union, Grand Ballroom

Organizer: P. Deshong

12:30 PM - 4:00 PM


12:30 PM  377.  Application of Constant Energy Synchronous Luminescence for Determination of Critical Micelle concentration of Selected Surfactants. **M. O. Iwunze**, M. O. Iwunze, M. O. Iwunze

12:30 PM  378.  Perchlorate SERS analysis using cysteamine-modified silver nanofilms – effects of pH and coexisting ions. **J. Hao**, M. Han, X. Meng

12:30 PM  379.  Silver nanostructured multilayer films for arsenate SERS sensing in contaminated groundwater. **M. Han**, **J. Hao**, X. Meng
12:30 PM  380. Speciation analysis and detection of arsenic in contaminated groundwater by surface-enhanced Raman scattering. M. Han, J. Hao, C. Christodoulatos, X. Meng

12:30 PM  381. Multiplex Detection of Tree Nuts in Food Using Real-time PCR. E. D. Mani-wang, E. A. Garber

12:30 PM  382. Analytical detection of nitroxyol (HNO) using membrane inlet mass spectrometry (MIMS). M. R. Cline, J. P. Toscano

12:30 PM  383. Cytosrchrome c unfolding in the presence of Cardiolipin bound phospholipid vesicles. S. Greer, J. Xi, R. Schweitzer-Stenner, J. Soffer


12:30 PM  386. Gas-phase chemiluminescence of arsine for the measurement of arsenic in water: Development of a routine analytical technique. K. Assegid

12:30 PM  387. SERS and DFT Study on Antitumor Active Derivative of 1, 4-naphthoquinone. M. Ukaegbu, A. Vivoni, O. Bakare, N. Enwerem, C. Hosten


12:30 PM  390. Challenges in the determination of soluble barium in D&C Red Nos. 6 and 7 lakes. N. Hepp, N. Belai


12:30 PM  394. Trace-level analysis of oxygen and moisture in specialty gas applications. S. Kidambi, J. Graehling

12:30 PM  395. 2-Hydroxy-1,4-Naphtnoquinone As An Electrochemical Anion sensor. Y. Zhang, Y. Hijji, B. Barare


Protein modifications of the ribosome in acquired drug resistance. K. L. Lohnes, F. Hays, J. Wolfe, A. Petrov, Y. Wang, J. Dinman, C. Fenselau

Microbial sequestration of carbon dioxide injected in the deep subsurface. A. Rienteau, D. Strongin, B. Van Aken

CO₂ sequestration through mineral carbonation of iron oxyhydroxides. K. D. Lammers, R. T. Murphy, A. Smirnov, M. A. Schoonen, D. R. Strongin


Measurement of Trace Arsenic in Groundwater by Reflectance Photometry. A. Hussam, J. Rozario

Lawson as a colorimetric anion sensor. Y. Hijji, B. Barare, Y. Zhang


Galvanic displacement as a rapid and simple method to fabricate surface enhanced Raman spectroscopy (SERS) substrates. J. F. Betz, Y. Cheng, O. N. Bekdash, G. W. Rubloff


Association of n-Alkylbenzenes with Fulvic Acid in Aqueous Media. M. D. Eljack


Computer numerical control (CNC) milling for rapid production of poly(dimethylsiloxane) (PDMS) microfluidic devices. J. M. Karlinsey

Direct Mass Spectrometry Screening of Pomegranate Juice Adulteration. L. K. Ackerman, S. MacMahon

Environmental Fate of Polyhexamethylene Biguanide. A. D. Lucas

Ultra-sensitive detection and effect of Hg(II) on cell membranes. M. A. Cheney, S. Qian

Argon and the pathophysiology of pulmonary oxygen toxicity. R. Shanklin

Chemical paint strippers: Understanding how methylene chloride and phenol remove polymeric coatings. K. E. Watson, J. H. Wynne, J. P. Yesinowski, Y. Han, C. N. Young, C. R. Clayton

Filtration of natural and synthetic estrogens using an activated charcoal solution. J. Wang, J. Field

Light-mediated oxidative decontamination on polyurethane coatings. J. G. Lundin, R. F. Cozzens, K. E. Watson, J. H. Wynne
12:30 PM 419. Evaluation of lime-stabilized biosolids as a soil amendment. **M. Guo**

12:30 PM 420. Removal of Chromium and Lead From Water by Sorption on Iraqi Montmorillonite. **M. M. Barbooti**

12:30 PM 421. Thiol compounds that bind heavy metals. **K. M. Zaman**

12:30 PM 422. Catalytic Electrochemical Reduction of \( \text{CO}_2 \) in Designed Ionic Liquid. L. L. Snuffin, L. W. Whaley, **L. Yu**

12:30 PM 423. Interactive internet database cataloguing descriptive information about botulism cases since 1793. **V. Tangri, S. Sharma**

12:30 PM 424. Determination of biologically active compounds in green tea dietary supplements. **M. Bedner, L. C. Sander, K. E. Sharpless**

12:30 PM 425. Membrane bioreactor process modeling and optimization by Artificial Neural Network and integrated bioprocess models. **J. C. Chen, R. Luo, S. Mu, Z. Zhang, M. Andersen, P. E. Jørgensen**


12:30 PM 428. Effect of Polyethylene glycol degradation on voiding, sporadically occurring in solder joints with electroplated copper. **F. Wafula, Y. Liu, L. Yin, P. Borgesen, N. Dimitrov**

12:30 PM 429. Spiral Countercurrent Chromatography: Advance in a classical technology. **M. Knight, T. M. Finn**


**Bioactive Small Molecule Design and Discovery**

**Drug Discovery**

Organizer: C. J. Thomas

1:00 PM 440. Introductory Remarks.


1:45 PM 442. Exploration of the Existing Drug Space for Novel Inhibitors of Angiogenesis. **J. O. Liu**

3:05 PM 443. Discovery of N-type calcium channel (Ca\textsubscript{v2.2}) blockers for the treatment of chronic pain. **J. L. Duffy**

3:45 PM 444. The NIH Therapeutics for Rare and Neglected Diseases Program. **J. McKew**

4:25 PM  Concluding Remarks.

**Expiration of Patent Protection: A Major Challenge Facing the Chemical and Pharmaceutical Industries in the 21st Century**

Stamp Student Union, Pyon Su Room
Organizers: K. Bianco, J. Hasford

1:00 PM  Introductory Remarks.

1:05 PM 445. Patent protection for chemists: An overview. **S. Cyr**

1:30 PM 446. Drafting winning patents that withstand written description and enablement challenges. **L. Feng**

1:55 PM 447. Patenting chemical products and processes – how double patenting can limit patent protection. **C. Hlavka**

2:20 PM 448. Damages for infringement of chemical patents. **J. Abraham**

2:45 PM 449. Patent term extensions after drug approval. **M. Chlebowski**

3:10 PM 450. Pharmaceutical patent timelines. **A. Sibley**

3:35 PM 451. Reconciling patent rights and public health issues: Implications of the TRIPS Agreement for the pharmaceutical industry. **K. Braslow**

4:00 PM 452. Proposed U.S. patent reform. **S. Jhaveri**

4:25 PM  Concluding Remarks.

**Metal-Mediated Small Molecule Activation and Functionalization Catalysis**

Stamp Student Union, Charles Carroll Room B
Organizer, Presiding: L. Sita

1:00 PM  Introductory Remarks.


2:50 PM  Intermission.


4:25 PM  458. Dinitrogen and carbon dioxide activation and fixation by groups 4 - 6 metal monocyclopentadienyl, monoamidinate complexes. B. L. Yonke, W. Farrell, J. Reeds, P. Y. Zavalij, L. R. Sita

Redefining the Kilogram and Avogadro’s Number
Chemistry Building, 1407
Organizer, Presiding: R. L. Watters

1:00 PM  Introductory Remarks.
1:10 PM  459. The International System of Units and Plans for its Redefinition. P. J. Mohr
1:50 PM  460. Overview of Watt Balance Experiments to Measure the Kilogram. R. L. Steiner
2:30 PM  Intermission.

3:25 PM  Concluding Remarks.

Ambient Ionization Methods for Biological Mass Spectrometry
Chemistry Building, 3219
Organizer: A. Vertes

1:30 PM  Introductory Remarks.
1:35 PM  462. Laser ablation electrospray ionization (LAESI) mass spectrometry for the analysis of single cells and tissues. A. Vertes, J. A. Stolee, B. Shrestha
2:35 PM  463. Development of a low power ion trap mass spectrometer for mars. R. J. Cotter, T. Evans-Nguyen, V. Pinnick
3:35 PM  Intermission.

4:45 PM  Concluding Remarks.

CFDV Student Award Symposium for Separation Science
Chemistry Building, 1402
Organizer: M. Selman

1:30 PM  Introductory Remarks.
1:35 PM  465. Enantiomeric separations of cationic and anionic pharmaceutical compounds using dual opposite injection capillary zone electrophoresis with neutral cyclo-dextrins. P. DeGregory, D. Blackney, J. P. Foley
1:55 PM 466. MEKC investigation of the chiral recognition capabilities of bile salt micelles. A. R. Meier, J. B. Yehl, D. Rovnyak, T. G. Strein

2:15 PM 467. Optimizing a short-end electrophoretically mediated micro-analysis (EMMA) assay for creatinine. A. C. Seneviratne, T. G. Strein

2:35 PM 468. Using Ferrocene For Improved LC-MS Detection of Arteriosclerotic Chlorinated Fatty Alcohols. C. M. Defendorf, J. R. Sowa, J. A. Bowden, D. A. Ford

2:55 PM Intermission.


3:30 PM 470. Development of a Project-based Laboratory Involving LC-MS to Introduce Students to Drug Discovery. J. M. Kontra, B. W. Parks, T. J. Peelen

3:50 PM 471. Transfer of thin layer chromatography pharmaceutical product screening methods designed for use in developing countries to quantitative High Performance TLC densitometry methods. C. O’Sullivan, J. Sherma

4:10 PM 472. Capillary and Microfluidic Gradient Elution Isotachophoresis Coupled to Capillary Zone Electrophoresis for Femtomolar Amino Acid Detection Limits. N. I. Davis, M. Mamunooru, C. A. Vyas, J. G. Shackman

4:30 PM Concluding Remarks.

Chemistry and Materials Composition of Cultural Heritage Materials
Chemistry of Art Conservation
Stamp Student Union, Juan Ramon Jimenez Room
Organizer: F. France

1:30 PM Introductory Remarks.

1:40 PM 473. Non-Invasive Spectral Imaging for Characterization of Cultural Heritage Materials. F. G. France

2:10 PM 474. Details of Mimbres Pottery Production and Distribution Revealed by INAA. R. J. Speakman, D. Creel, M. R. Miller

2:40 PM Intermission.

2:55 PM 475. Archaeological approach to the analysis of cultural heritage in library collections. L. B. Brostoff, K. Gaskell


4:25 PM Concluding Remarks.
### Food Safety: New Technologies for the Protection of the Food Supply II

**Food Safety**  
Stamp Student Union, Benjamin Banneker Room A  
Organizers: K. Morehouse, B. Yakes

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<tr>
<th>Time</th>
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<th>Presenter(s)</th>
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<td>1:30 PM</td>
<td>Introductory Remarks.</td>
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<tr>
<td>1:40 PM</td>
<td>478. Alternative Food Safety Intervention Technologies. <strong>C. Sommers</strong></td>
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<td>2:05 PM</td>
<td>479. Evolution of compendial testing standards for food ingredients to guard against economically motivated adulteration. <strong>J. C. Moore</strong></td>
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<td>2:30 PM</td>
<td>480. Analysis of organic acids in fruit juices by liquid chromatography - mass spectrometry: An enhanced tool for authenticity testing. <strong>S. Ehling, S. Cole</strong></td>
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<td>2:55 PM</td>
<td>481. Chemometric Analysis of Mass Spectral Fingerprints for Authentication and Quality Assessment of <em>Scutellaria lateriflora</em> and Dietary Supplements. <strong>P. Chen, J. Sun, J. Harnly</strong></td>
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<td>Intermission.</td>
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<td>3:40 PM</td>
<td>482. Determination of carbon black in food products. <strong>E. Miranda-Bermudez, N. Belai, B. Petigara Harp, B. Yakes, J. N. Barrows</strong></td>
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<td>4:30 PM</td>
<td>484. Surface plasmon resonance biosensors for enhancing food safety. <strong>B. J. Yakes, S. L. DeGrasse</strong></td>
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<td>4:55 PM</td>
<td>Concluding Remarks.</td>
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### New Technologies for Lithium Ion Batteries II

**Polymer Chemistry**  
Stamp Student Union, Charles Carroll Room A  
Organizer, Presiding: P. Kofinas

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<td>2:10 PM</td>
<td>486. Ionic liquid-based electrolytes for lithium batteries: Linking structure with electrolyte properties. <strong>W. Henderson, Q. Zhou, J. Weaver</strong></td>
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<td>3:00 PM</td>
<td>Intermission.</td>
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<tr>
<td>3:55 PM</td>
<td>488. Electrolyte in support of 5-volt lithium ion battery systems. <strong>A. V. Cresce, K. Xu</strong></td>
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<td>4:35 PM</td>
<td>Concluding Remarks.</td>
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ABSTRACTS

Chromatography

1. GCxGC-ToFMS: A Chromatography Sandbox

Nicholas H Snow(1), nicholas.snow@shu.edu, 400 South Orange Avenue, South Orange NJ 07079, United States. (1) Department of Chemistry and Biochemistry, Center for Academic Industry Partnership, Seton Hall University, South Orange NJ 07079, United States

Comprehensive two-dimensional gas chromatography combined with mass spectrometry (GCxGC-ToFMS) provides extremely high chromatographic resolution combined with the sensitivity and rapid scanning of time of flight mass spectrometry. In GCxGC, the effluent from a traditional first dimension capillary column is sampled, focused and injected into a short second dimension column of differing polarity. The resulting two-dimensional chromatogram has increased peak capacity resulting from the multiple separation mechanisms. The myriad applications of GCxGC-ToFMS have only begun to be explored. The separation ability of GCxGC will be discussed using pharmaceutical solvents as an example. The powerful qualitative analysis possible when combined with ToFMS will be described with complex crude oil samples. Finally, the extreme separation power of GCxGC-ToFMS when combined with a selective extraction such as solid phase micro-extraction will be demonstrated by the analysis of drugs of abuse from water and urine. GCxGC-ToFMS is a very powerful separation tool: the gas chromatographer’s sandbox.

2. Electrostatic Interactions and the Implications on Peak Tailing of Bases

Brian Bidlingmeyer(1), brian_bidlingmeyer@agilent.com, 2850 Centerville Road, Wilmington DE 19808, United States. (1) Agilent Technologies, Inc., United States

Tailing of chromatographic peaks for basic compounds have been a concern for researchers since the early years of chromatography. It is clear that retention of basic compounds (+ charge) is retained longer on bonded phases at pH 7 due to the electrostatic interactions with the unreacted silanols. Further, it is generally believed that this electrostatic interaction is also responsible for tailing; and, it is generally believed that at low pH peaks are tailed less than at pH 7. However, we have observed that this is not always the case. What is the case at low pH is that peaks have less retention and appear sharper; but, in actuality tailing does exist at pH 2 and tailing can be better at pH 7. Why is this?

This work investigates observations made at pH=2 & 7 and suggest a possible explanation as to why the peak shapes can be more tailed at pH 2. In its simplest form the cause of tailing is due to the molecules in the band center remaining longer in the mobile phase. Thus, molecules migrate faster than those of lower concentration in the band extremities. This principle is expanded into a hypothesis as to the cause of the observations. The effect of mobile phase additives on tailing is demonstrated which support the hypothesis for the cause of tailing. Additionally, observations are made concerning the evaluation of tailing at pH 7 which suggest that attempting to use a single probe to predict universal behavior may be a futile effort.

3. Chromatographic applications and beyond in the Agricultural Industry

Mary Ellen P. McNally(1), mary-ellen.mcnally@usa.dupont.com, Stine Haskel Research Center S315/2224, 1090 Elkton Road, Newark DE 19711-3507, United States. (1) Crop Protection Products, Stine Haskell Research Center, E.I. DuPont de Nemours & Co., Inc., Newark DE 19711, United States

In the agricultural industry, discovery and development rely heavily on analytical chemistry and specifically separation science. From the first positive field response to the commercial scale-up of a crop protection product a variety of chromatographic and separation techniques are used. This presenta-
tion, will outline the process of taking a product through the development process from an analytical chemistry perspective. Technologies using radiolabeled materials, LC/MS, the Geno Grinder, UPLC and HPLC will be illustrated. Method transfer essentials will also be discussed.

**Metallation Chemistry**
**Organizers:** P. Deshong, V. Snieckus

**4. Functionalization of C(sp3)-H Bonds for Synthesis of Complex Molecules**

*Gong Chen* (1), guc11@psu.edu, 104 Chemistry Building, University Park PA 16802, United States. (1) Chemistry, Penn State University, University Park PA 16802, United States

Despite the tremendous advances made over the last two decades and the great potential of C−H functionalization, its application in organic synthesis is still limited. There are pressing reasons to push C−H functionalization to the front line of organic synthesis, namely truly practical and generally applicable synthetic methods capable of versatile transformations and their utilization in complex molecule synthesis. These synthetic methods must be highly selective and predictable in terms of both regio- and stereo-control. The methods need to be operationally simple, take place under mild reaction conditions, and tolerate a large range of functional groups. In this talk, we will present our recent development of practical and efficient synthetic methodologies based on the Pd-catalyzed amidate-directed selective functionalization of C−H bonds. Two types of general reaction strategies based on the primary amine groups will be discussed. While these methodologies can be widely applied toward the goal of structural diversification synthesis for medicinal chemistry research, we will demonstrate their synthetic utility in the context of synthesis of natural product celogentin C and (+)-obafluorin.

**5. Stereoselective Palladium-Catalyzed [2,3]-Stevens Rearrangement**

*Arash Soheili* (1), arash.soheili@utsouthwestern.edu, 5323 Harry Hines Blvd, Dallas TX 75219, United States; Uttam K. Tambar (1). (1) Biochemistry, University of Texas Southwestern Medical Center, Dallas TX 75219, United States

We have developed a cross-coupling reaction between aminoesters and allylcarbonates, which constitutes the first example of using tertiary amines as intermolecular nucleophiles in metal-catalyzed allylic substitution chemistry. This process is employed in a tandem ammonium ylide generation / [2,3]-rearrangement, which formally represents a palladium-catalyzed Stevens rearrangement.

Low catalyst loadings and mild reaction conditions are compatible with unprecedented substrate scope for ammonium ylide functionality and products are generated with high yields and diastereoselectivities.
6. Oxidative C-C bond formation mediated by a hypervalent iodine reagent: Developments and applications

**Sylvain Canesi** (1), canesi.sylvain@uqam.ca, C.P. 8888, Succ. Centre-Ville, Montreal Quebec H3C 3P8, Canada. (1) Department of Chemistry, Universite du Quebec a Montreal, Montreal Quebec H3C 3P8, Canada

Electron-rich aromatic compounds, such as phenols and their derivatives, are involved in different biosynthesis of natural products. These compounds normally react as nucleophiles; however, an oxidative activation mediated by a hypervalent iodine reagent, an environmentally benign reagent, can transform these aromatics into very reactive electrophilic species, which may be intercepted with appropriate carbon based nucleophiles. This reversal of reactivity may thus be thought of as involving “aromatic ring umpolung”. This concept provides new strategic opportunities in synthetic chemistry, performed by a dearomatizing strategy and by extension of several well known reactions in aliphatic chemistry to the aromatic chemistry. In this presentation, several novel methodologies generating carbon-carbon bonds, will be described. These methods involve novel processes, such as an unprecedented Prins reaction, or several oxidative transpositions. In addition, different applications in total syntheses will be discussed, including an asymmetric formal synthesis of (−)-platensimycin (antibiotic), using an oxidative Prins-pinacol process as a key step.

7. 1,2,3-Triazole: Unique ligands in metal coordination and catalysis

**Xiaodong Michael Shi** (1), xiaodong.shi@mail.wvu.edu, 3 Vanessa Lane, Morgantown WV 26505, United States. (1) Chemistry, West Virginia University, Morgantown WV 26506, United States

Regioselective 1,2,3-triazole functionalization methods were developed, which allowed the application of specific triazole derivatives to be applied as ligands in transition metal coordination. The triazole complexes of Rh, Au, B, Ir and Fe were developed. Interesting reactivity of these complexes were revealed by tuning the transition metal catalytic and as novel reagents in important transformations.

8. Progress Toward the Total Synthesis of Angustilodine, Alstilobanine A, and Alstilobanine E

**Max M Majireck** (1), maxmajireck@hotmail.com, 104 Chemistry Building, Box 231, University Park PA 16801, United States; **Steven M Weinreb** (1). (1) Chemistry, Penn State University, University Park PA 16802, United States

The recently isolated natural products alstilobanine A (6), alstilobanine E (7), and angustilodine (8) belong to a new and unique skeletal-type of monoterpene indole alkaloids. A concise strategy for the total synthesis of these three alkaloids has been developed which involves conjugate addition of the dianion of indole-2-acetic acid methyl ester 1 to the nitrosoalkene generated from α-chlorooxime 2.
Additionally, application of Romo’s intramolecular aldol-lactonization methodology to forge the cis-azadecalin core provided pentacyclic \( \beta \)-lactone \( 4 \) and execution of a silicon-tethered intramolecular ester enolate alkylation provided the late-stage intermediate \( 5 \) which will be used to complete the synthesis of all three alkaloids.

**Medicinal Chemistry and Chemical Biology of Anticancer Agents**

Organizers: J. Talisman, S. Malhotra

9. Synthesis of hetero-polycyclic compounds using formal \([4+1]\)-cycloadditions

*Claude Spino*\(^{(1)}\), Claude.Spino@USherbrooke.ca, 2500 Boul. Université, Sherbrooke QC J1K 2R1, Canada; *Francis Beaumier*\(^{(1)}\); *Luc Boisvert*\(^{(1)}\); *Hadi Rezaei*\(^{(1)}\); *Louis-Philippe D.Lefebvre*\(^{(1)}\); *Martin Déry*\(^{(1)}\); *Kevin Aissa*\(^{(1)}\). (1) Chemistry, University of Sherbrooke, Sherbrooke QC J1K 2R1, Canada

The \([4+1]\)-cycloaddition between a carbene and a diene (1) is a reaction infrequently reported in the chemical literature. More often than not, the cyclopentene product \( 2 \) is the result of a formal cycloaddition, via cyclopropane \( 3 \) or another intermediate. We will present two different carbene/diene systems 1 that give good-to-excellent yields of the \([4+1]\)-cycloadducts 2 and discuss the scope and mechanism in each case.

10. Caged nitric oxide (NO) prodrugs: A platform for broad-spectrum drug discovery

*Larry K. Keefer*\(^{(1)}\), keeferl@mail.nih.gov, Building 538, Frederick Maryland 21702, United States. (1) Laboratory of Comparative Carcinogenesis, National Cancer Institute, Frederick Maryland 21702, United States

Rational drug design based on detailed physicochemical characterization of molecules containing the NO-releasing diazeniumdiolate \([-N(O)NO]-\) group, also known as “NONOates”, has yielded promising approaches to protecting the liver from toxic exposures, promoting wound healing after surgery, and treating cancer, among other prospective clinical applications. In this presentation, I will review the basic chemistry of these compounds and then illustrate how knowledge thereof can be exploited for selectively targeting bioactive NO to specific bodily compartments for therapeutic benefit. Emphasis will be on the anti-cancer activity of diazeniumdiolates designed to be activated for NO release by reaction with cellular nucleophiles such as glutathione.
11. D-peptide activators of the p53 tumor suppressor for anticancer therapy

Wuyuan Lu(1), wlu@ihv.umaryland.edu, 725 West Lombard Street, Baltimore MD 21201, United States; Changyou Zhan(1); Le Zhao(1); Weirong Yuan(1); Marzena Pazgier(1). (1) Institute of Human Virology and Department of Biochemistry and Molecular Biology, University of Maryland School of Medicine, Baltimore MD 21201, United States

The oncogenic E3 ubiquitin ligase MDM2 inactivates the tumor suppressor protein p53 by targeting it for proteasomal degradation. In many tumors harboring wild type TP53, MDM2 is amplified and/or over-expressed, conferring tumor development and progression. Inhibitors of the p53-MDM2 interaction rescue p53 from MDM2-mediated functional inactivation and kill tumor cells by reactivating the p53 pathway. We have recently reported the identification by mirror image phage display coupled with native chemical ligation several duodecimal D-peptide antagonists of MDM2, termed DPMI-α, DPMI-β and DPMI-γ, with \( K_D \) values ranging from 30 to 220 nM. When delivered intracellularly via a liposomal vehicle, these D-peptide inhibitors effectively suppress tumor growth of human glioblastoma in cell cultures and murine xenograft models. Based on the crystal structures of DPMI-α and DPMI-γ complexed with the p53-binding domain of MDM2, DPMI-β (TAWYANFEKLLR) has been functionally optimized through additional side-chain modifications, resulting in the most potent peptidomimetic inhibitor of the p53-MDM2 interaction reported to date.

12. Advances in the anticancer properties of semisynthetic artemisinin dimers

Andrew S Rosenthal(1)(2), rosenthalas@mail.nih.gov, 9800 Medical Center Drive, Building B, Room 3005, Rockville MD 20850, United States; Gary H Posner(2). (1) Chemical Genomics Center, National Institutes of Health, Rockville MD 20850, United States (2) Department of Chemistry, Johns Hopkins University, Rockville MD 20850, United States

The recently FDA approved drug, artemisinin, was discovered centuries ago as a naturally occurring plant in China. Although classically used as an herbal remedy for malaria, the highly stable trioxane has been found to have potent \textit{in vivo} antiproliferative and anticancer activities. Semisynthetic C-10 non-acetal artemisinin dimers have been shown to be more effective than doxorubicin in treating human prostate cancer cells and are safe and non-toxic in short term oral dosing studies in mice. Recent \textit{in vitro} studies have revealed potent activity of artemisinin dimers against leukemia, melanoma, lymphoma and cervical cancer cells. A variety of monomer and dimer artemisinins have the ability to inhibit cytomegalovirus (CMV) replication, which can prevent future tumor formation in infected patients. The versatility of this complex natural product is being explored and expanded upon to improve quality of life in those suffering from a wide range of cancers.
13. Small molecule modulation of the Lysophosphatidic acid pathway in the treatment of neoplastic growth

James E East\(^{(1)}\), je5y@virginia.edu, PO Box 400319, Charlottesville VA 22902, United States; Kevin R Lynch\(^{(2)}\); Timothy L Macdonald\(^{(1)}\). (1) Department of Chemistry, University of Virginia, Charlottesville VA 22902, United States (2) Department of Pharmacology, University of Virginia, Charlottesville VA 22902, United States

Lysophosphatidic Acid (LPA) is an endogenous phospholipid signaling molecule implicated in a myriad of neoplastic disease states including breast and prostate cancer. LPA contributes to these diseases due its role in numerous biological processes such as angiogenesis, cell proliferation, migration and invasion. LPA is synthesized from lysophosphatidylcholine (LPC) by the Nucleotide Phosphatase/Pyrophosphatase 2 (NPP2) enzyme Autotaxin (ATX). Once synthesized by ATX, LPA goes on to act on one of five LPA Receptors (LPA1-5). These receptors are classical G-protein coupled receptors (GPCRs) that are responsible for Ca\(^{2+}\)mobilization and increasing MAP kinase and phosphatidylinositol bisphosphate (PIP2) pathway activities. Our labs have developed two small molecules derived from L-tyrosine: one, VPC8a202, that inhibits the synthesis of LPA while the other, VPC51299 blocks the signaling of the LPA1 and LPA3 receptors. These compounds are not only efficacious in \textit{in vitro} studies but have been shown to reduce tumor size and metastasis \textit{in vivo}.

14. Design, synthesis, and biological evaluation of RSK inhibitors

Michael K Hilinski\(^{(1)}\), mh6cu@virginia.edu, PO Box 800577, Charlottesville VA 22908, United States; Bulan Wu\(^{(2)}\); George A O'Doherty\(^{(2)}\); Deborah A Lannigan\(^{(1)}\). (1) Department of Microbiology and Center for Cell Signaling, University of Virginia School of Medicine, Charlottesville VA 22908, United States (2) Department of Chemistry and Chemical Biology, Northeastern University, Boston MA 02115, United States

The Ser/Thr protein kinase family, RSK (p90 ribosomal S6 kinase), functions in both normal homeostasis and disease states, including breast and prostate cancer, in which it is overexpressed in \(~50\%\) of tumors relative to normal tissue. One isoform, RSK2, regulates the expression of cyclin D1 in breast tumor cell lines but not in normal cell lines. Consistent with this observation, treatment with SL0101, a small molecule inhibitor of RSK, leads to inhibition of growth of transformed but not normal cell lines. SL0101 is a kaempferol glycoside isolated from the tropical plant \textit{Forsteronia refracta}, initially identified from a high-throughput screen of botanical extracts. It is the most specific inhibitor of RSK yet identified.

Our current studies are focused on the design, synthesis, and biological evaluation of derivatives of SL0101 that improve on its potency and membrane permeability. Through a first set of analogues we determined that the kaempferol hydroxyl groups are crucial for potency, and that the 3” and 4” acetates of the rhamnose portion of the molecule are important for both potency and specificity for RSK. Replacements for the acetates that were more lipophilic conferred an increase in membrane permeability, but specificity of RSK inhibition was reduced. To design a next set of analogues we turned to...
computer-aided docking studies. RSK is an unusual kinase, containing two functional, non-identical kinase domains, both an N-terminal (NTKD) and a C-terminal (CTKD) kinase domain connected by a linker. SL0101 is an ATP-competitive inhibitor of the NTKD of RSK, which is responsible for phosphorylation of exogenous substrates and belongs to the AGC kinase family. The closest relative of the RSK2 NTKD, p70 S6 kinase, adopts a canonical kinase structure that places an α helix (αC-helix), which contains residues important for the activation of ATP, near the ATP binding site. Interestingly, the crystal structure of the isolated active NTKD of RSK2 adopts a different conformation, in which a β-sheet displaces the αC-helix. This non-canonical crystal structure was used as the basis for docking studies of SL0101 and its analogues and was found to be consistent with known structure activity relationships and also predictive in the case of analogues that contain varying substitution at the 5″ position of the rhamnose portion of the molecule. This model is currently being used to develop analogues of SL0101 that would be suitable for evaluation in animal models of cancer.


Oleh Taratula(1), oleht@pegasus.rutgers.edu, 160 Frelinghuysen Road, Piscataway NJ 08854, United States; Olga Garbuzenko(1); Alex M Chen(1); Zuocheng Wang(2); Gediminas Mainelis(2); Tamara Minko(1). (1) Department of Pharmaceutics, Rutgers, The State University of New Jersey, Piscataway NJ 08854, United States (2) Department of Environmental Sciences, Rutgers, The State University of New Jersey, New Brunswick NJ 08901, United States

Conventional chemotherapy usually employs high doses of toxic drugs which often induce severe adverse side effects on healthy organs. In addition, the efficacy of chemotherapy is also limited by the rapid development of tumor resistance. Therefore, to enhance lung cancer treatment, we developed an efficient nanomedicine platform based on Mesoporous Silica Nanoparticles (MSNs) for inhalation local delivery of anticancer drugs in combination with MRP1 and BCL2 targeted siRNAs as suppressors of pump and nonpump cellular resistance, respectively. Thiol-functionalized MSNs were synthesized by using a surfactant-templated, base-catalyzed condensation method by following post-modification of particle surface. The prepared particles have large surface areas (1000 m²/g) and pore size (2.95 nm) that can be used as reservoirs for storing hydrophobic anticancer drugs. Doxorubicin was encapsulated into the pores of MSN, while thiol-functionalized siRNAs and polyethylene glycol (PEG) were chemically conjugated to the surface of MSNs via cleavable disulfide bonds. Furthermore, LHRH peptide was attached to the distal end of PEG to direct the delivery system (DS) specifically to the lung cancer cells and limit the cytotoxic effect of chemotherapy on healthy organs. In vitro study demonstrated the feasibility of the developed DS to sufficiently enhance delivery of Doxorubicin and siRNAs into human A549 lung cancer cells. Inhalation co-delivery of the developed DS into nude mice with an orthotopic model of human lung cancer substantially improved lung exposure to the active components and limited their accumulation in other organs when compared with intravenous administration. Moreover, targeting DS specifically to lung cancer cells enhanced the accumulation of DS in the lung tumor. Our results demonstrate high capability of MSNs to deliver their payload specifically to lung cancer tumor, substantially enhance the efficacy of lung cancer treatment and limit adverse side effects of chemotherapy on healthy organs.

16. Structure activity studies of antiproliferative factor: A novel glycopeptide negative growth factor from interstitial cystitis patients

Joseph J Barchi(1), barchi@helix.nih.gov, 376 Boyles Street, PO Box B, Frederick MD 21702, United States; Kristie M Adams(1); Susan Keay(2); Piotr Kaczmarek(1). (1) Chemical Biology, NCI Frederick, Frederick MD 21702, United States (2) Department of Medicine, University of Maryland, Baltimore MD 21202, United States

Interstitial Cystitis/Painful Bladder Syndrome (IC/PBS) is a chronic bladder disorder characterized by severe pain caused by thinning and ulceration of the bladder wall. Interestingly, urine specimens from approximately 95% of IC/PBS patients contained an antiproliferative factor (APF) that induces...
many of the same abnormalities in normal human bladder epithelial cells in vitro as seen in IC/PBS cells, suggesting a primary role for this agent in the pathology of IC/PBS. APF was identified as a sialylated glycononapeptide, viz. Neu5Acα2-3Galβ1-3GalNAc-α-O-TVPAAVVVA with a very intriguing structure-activity profile. Further studies revealed APF is also able to inhibit proliferation of different cancer lines at low nanomolar concentrations. Thus, APF is a new and unique lead in IC/PBS and anticancer therapeutic research. The presentation will discuss the chemistry and biology of APF and our efforts to define the detailed SAR of this fascinating negative growth factor.

New Approaches to Teaching Chemistry I
Organizer: S. Sinex

17. Teaching and learning in the digital age: Chemistry resources teachers and students can rely on from the ChemEd DL

Linda Fanis(1), lnfanis@wisc.edu, 1101 University Avenue, Madison WI 53706, United States; John W. Moore(1). (1) ChemEd DL, Madison WI 53706, United States

Digital resources play an increasingly dominant role in teaching and learning chemistry. However, of paramount importance is that a teacher can be certain that the digital resource will work reliably, that it is useful, and that it is accurate. The Chemical Education Digital Library (ChemEd DL) collection provides exemplary digital resources, tools, and online services to aid in teaching and learning chemistry at all levels. During our hands-on guided workshop participants will be introduced to the ChemEd DL’s newest releases from their innovative collection of free digital resources. The updated collection includes the interactive Periodic Table Live! version 2.0 with videos of the elements and the ability to graph periodic properties; Models 360, an expansive Jmol collection of organic and small inorganic molecules useful for teaching VSEPR, polarity, bond length and more; and the ChemTeacher collection designed especially for high school teachers wanting to find demos, videos, articles and worksheets searchable by topic and the science standards. Participants will learn how they can use and access these resources from home as well as contribute their own materials to the collections.

18. NMR determination of hydrogen bond thermodynamics in a dipeptide model: A physical chemistry experiment

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Variable temperature NMR spectroscopy is used to determine the ∆H° and ∆S° of hydrogen bond formation in a dipeptide model. In this two-day experiment, students synthesize N,N’-dimethylmalonamide from methylamine and dimethylmalonate (typically in 50% recrystallized yield) and record NMR spectra at temperatures between 200 and 298K. Solutions of N-methylacetamide in concentrations varying between 1.00 mM to 13.1 M (neat) are prepared and their NMR spectra recorded in order to determine the chemical shift of the amide proton in the hydrogen-bonded (δb) and non-bonded (δn) limits. Using this data, the equilibrium constant for the formation of an intramolecular hydrogen bond is obtained. A van’t Hoff plot of lnK vs. 1/T allows for the determination of ∆H° (-3.21 ± 0.07 kJ/mol) and ∆S° (-9.96 ± 0.28 J/mol•K). We have also studied the corresponding diamide derivatives from diethyl succinate (n=2), glutarate (n=3), and adipate (n=4) in order to evaluate entropic effects of ring size in this system.
19. **Analysis of student performance on multiple-choice questions in general chemistry**

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The percentage of students choosing the correct answer (PSCA) on 17 multiple-choice algorithmic questions taken from general chemistry exams is analyzed. PSCAs for these questions varied from 47-93% and a decrease of 4.5% in PSCA was observed with each additional step in the algorithm required for solving the problem ($R^2 = 0.80$). Variants of a subset of these questions were also examined and reveal the effect of making changes to a particular algorithmic question on the ability of students to choose the correct answer.

20. **Dominant visuo-spatial techniques in the organic chemistry classroom**

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As in all the sciences, the ability to mentally generate and manipulate spatial images is essential to problem solving in organic chemistry. A central component of organic chemistry revolves around the connection between molecular shape and function, and so the abilities to imagine and work with molecules in 3D, as well as proficiency in translating these molecules to 2D images, are critical skills for young chemists to gain. In classrooms, instructors will often demonstrate the three-dimensionality of molecules using physical models. Through the manipulation and handling of these models, students are able to establish connections between 3D molecules and 2D diagrams of these molecules. While investigating students’ abilities to draw 2D Newman diagrams from 3D models in a lecture hall setting, we have observed significant evidence of specific visuo-spatial practices employed by students faced with this task. For example, students prefer to depict the left-side stereocenter of a dash-wedge molecule as the front of a Newman diagram, even though it is equally acceptable to illustrate the right-side stereocenter at the front of the Newman diagram (see figure). Many instructional techniques and textbooks are found to exacerbate this partiality in spatial manipulation. Most interestingly, use of these dominant spatial practices was found to be significantly correlated with overall success. The cognitive psychology community has observed a link between written language and the propensity to approach temporal relationships in the same direction used when writing. Others claim dominant directionality exists within non-spatial elements, such as time and mathematics, although we have found no reports of similar findings in the scientific education community. The impact of such a spatial preference in the chemistry classroom, and the debate of whether to promote its use, will be discussed.
21. **Green chemistry educational materials and opportunities**

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The ACS Green Chemistry Institute® (ACS GCI) has been helping educators incorporate green chemistry into the chemistry curriculum for over ten years. In partnership with the Education Division at the American Chemical Society (ACS) as well as with green chemistry educators, ACS GCI has recently developed several new educational books and online tools. The presentation will provide an overview of these resources as well as opportunities for students and educators, including as awards, travel funding, and training workshops.

22. **Conceptual thinking versus plug-and-chug problem solving: Radiocarbon dating and interactive animated spreadsheets**

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Radiocarbon dating is a Nobel Prize winning, practical application of chemistry that is used in the Earth sciences and anthropology. Most general chemistry textbooks do a lack-luster job of explaining methods and their assumptions but jump right into mathematical equations and a variety of plug-and-chug problems. We illustrate a dynamic, conceptual approach using pre-built animated spreadsheets to investigate the process. A number of the assumptions and uncertainties of radiocarbon dating are explored and discovered by students. Students need to know the basics of mathematical modeling, another valuable skill, to predict-test-analyze and then explain and deal with error analysis. Students address many higher-order “what if” questions and use a variety of science process skills to develop a deeper conceptual understanding.

23. **Description of a nontraditional freshman-sophomore chemistry sequence and an analysis of student performance**

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Starting in the fall of 1996, freshman science majors at Wesley College began following a revised nontraditional chemistry sequence, in which General Chemistry I in the fall of the freshman year is followed by Organic Chemistry I in the spring. Students continue with Organic Chemistry II in the fall of the sophomore year, and complete the sequence the following semester with General Chemistry II. In addition, to provide students with a greater exposure to chemistry, the first semester Biology I course is postponed from the fall semester of the freshman year to the following spring semester. This presentation will concentrate on the general chemistry portion of the sequence, especially changes in the nature and depth of presentation of topics in the General Chemistry I course, compared to those in the traditional general chemistry sequence. Advantages and disadvantages of this sequence will be discussed. A comparison of student grade performance in the new vs. the old sequence will also be presented. Performance in both General Chemistry I and Biology I is not significantly different in the two sequences. Significant differences are found, however, in student performance in both Organic Chemistry I and General Chemistry II.
24. Woodward-Fieser rules on Excel spreadsheets

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Two spreadsheets that can be used to predict the UV wavelength of maximum absorption will be demonstrated. One of them predicts the wavelength of maximum absorption for conjugated dienes, and the other predicts it for alpha, beta-unsaturated aldehydes or ketones. Students are introduced to the fundamentals of UV spectroscopy in general chemistry. This allows them to proceed to practical applications of UV in their organic courses. Learning and applying the Woodward-Fieser rules to conjugated systems is quite in keeping with a major theme of first-semester organic chemistry: structure begets properties. The spreadsheets allow students to see how the property of maximum wavelength varies with structure without having to memorize the effect of each structural feature. Instead, they can focus on learning the structural features (e.g., endo- or exocyclic double bonds, extended conjugation, etc.) that give rise to the changes in wavelength.

25. Improving feedback from clicker questions

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Personal response devices (or clickers) continue to be used to improve classroom engagement and student learning. However, multiple choice questions do not always provide the desired information. Sometimes the choices enable students to guess the correct answer without a complete understanding of the concept. In order to address this problem, clicker questions have been redesigned to improve the feedback provided for the instructor and the students in General Chemistry classes. Two new question types will be described. First, multiple response questions give students the ability to submit more than one correct answer, which eliminates the option to simply choose the best answer. Second, process-based questions ask students to identify what equations are needed to perform a calculation. Results of each question type will be presented to demonstrate the improved feedback. The new question types enable the identification of points of confusion that had not been identified by single-answer questions.

26. Dissecting the structure-mechanism-reaction paradigm of organic chemistry in a 100-student course with personal response systems (‘clickers’): is ‘structure’ a threshold concept?

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Organic chemistry courses typically follow a paradigmatic sequence that starts with the structure and properties of organic molecules, an introduction to one or more examples of mechanisms of organic reactions, after which the majority of class time is devoted to the synthesis and reactions of the various functional groups. The beauty of organic chemistry as a predictive science is that knowledge of structure determines the allowed mechanistic pathways, from which the reaction outcome – the products – can be confidently predicted. One barrier a student must overcome if they are to successfully master this ‘structure-mechanism-reaction’ paradigm is their (in)ability to draw mechanism arrows – the symbolic flow of electrons that represent the proper conversion of reactants to products. A recent publication (Ruder and Straumanis, J. Chem. Educ., 2009, 86, 1392-1396) described the use of personal response systems (‘clickers’) to create a numeric representation of organic chemistry mechanism arrows. This publication prompted us to use clickers as a probe of student understanding of organic chemistry mechanisms. The focus of this talk will be on how to use clickers in the classroom to represent electron-flow arrows, their impact on performance on
mechanism-based exam questions, and whether it is knowledge of structure or ability to draw mechanisms that is the better predictor of overall course performance.

Protein Structure and Dynamics
Organizer: T. Dayie

27. Detection of protein conformational Intermediates by NMR relaxation
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During the past two decades, advances in Nuclear Magnetic Resonance (NMR) and its related technologies have tremendously increased the sensitivity of NMR relaxation experiments. Parameters obtained by NMR relaxation experiments have now sufficient sensitivity to provide information about internal dynamics associating to configurational energetics in proteins, and about insights in to the site specific information involved in conformational equilibriums. However, for meaningful results to emerge and for reasonable comparison of NMR-derived dynamics with those obtained by other methods, accurate evaluation of uncertainties in the NMR-derived parameters is critical. We are estimating or if possible to reduce, errors involved in the NMR relaxation experiments that are often used to characterize protein dynamics. We will talk about some of such efforts to reduce errors in the NMR relaxation, and recent application of the NMR relaxation experiments to detect conformational intermediate of a calcium binding protein, recoverin.

28. From NMR information to high accuracy biomolecular structures: A quantum chemical pathway
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NMR spectroscopic properties are sensitive probes to investigate biomolecules. Deciphering the NMR observable information through high accuracy quantum chemical calculation can provide valuable insights into structural investigations and related drug discovery. Recently, the use of the solid-state NMR chemical shift information of an FPPS×IPP×Risedronate complex (FPPS: farnesyl pyrophosphate synthase; IPP: isopentyl pyrophosphate; Risedronate: a drug molecule) together with quantum chemical investigations of model systems has assisted in refinement of the x-ray structure of this protein complex and revealed unprecedented structural information. Results also helped the discovery of new drug leads. More recently, our investigation of the solution NMR and other spectroscopic properties of the myoglobin complex with HNO, a small molecule that has recently been recognized to regulate many biomedical activities, uncovered the first atomic level binding details, which not only provides the best predictions of experimental spectroscopic measurements, but also offer novel insights into the reactivity and stability. Quantum chemical investigations of NMR hyperfine shifts have also aided the structural investigations of some paramagnetic protein systems and suggest that the NMR spectroscopic tool may supply sensitive structural information of the binding of redox active metals in the proteins involved in neurodegenerative diseases.
29. **Structural and Dynamics Studies of Microtubule-Associated Proteins by Magic Angle Spinning NMR Spectroscopy**

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We will discuss our recent progress in understanding structure and dynamics of microtubule-associated proteins CAP-Gly domain of dynactin and DLC8. We will introduce new MAS NMR techniques recently introduced in our laboratory that permit to overcome the sensitivity and resolution challenges in working with protein assemblies.

30. **Sensitivity enhancement by nonuniform sampling: theory and applications**

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Nonuniform sampling (NUS) has been increasingly employed in the acquisition of nD-NMR spectra, coupled with an array of methods for performing spectral estimation from the incompletely sampled data. Commonly cited benefits of NUS include the time savings that can be realized. In contrast less attention has been given to the sensitivity considerations of NUS. We present the first exact analytic theory for contrasting the signal-to-noise ratio for exponentially weighted NUS of decaying NMR signals to uniform sampling. These results indicate conditions for fundamentally improving sensitivity up to two fold, particularly when it is necessary to simultaneously optimize resolution. Applications in both small molecule and protein NMR spectroscopy will be shown which demonstrate that NUS can be employed to change the detection limit of NMR. This enhancement compared to uniform sampling is fundamental to the NUS approach under the assumption of equal experimental times and is independent of the spectral estimation method, can be combined with specialized hardware, and can be compounded in additional indirect dimensions. More broadly, these results eliminate the guesswork and uncertainty in evaluating the sensitivity considerations of NUS and allow for the rational design of NUS nD-NMR experimentation.

**Supramolecular Chemistry**

Organizer: J. Davis

31. **Targeted Xenon-Cryptophane Biosensors for Molecular Imaging**

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Nonproton-based hyperpolarized MRI biosensors are promising agents for early disease detection, especially when their interactions with target biomolecules can perturb chemical shifts well beyond the typical field inhomogeneity of clinical MRI (for example, in $^{129}$Xe NMR). We have developed biosensors based on cryptophanes with the highest reported affinity for xenon, a non-toxic contrast agent. Besides developing an efficient shorter 6-step synthesis for trifunctionalized cryptophanes, we have also demonstrated the specific cell uptake of cryptophane biosensors modified with specific targeting moieties to bind proteins upregulated in cancer cells. In addition, human carbonic anhydrase (CA), highly overexpressed in many types of cancer, was chosen as a single-binding-site enzyme for studying xenon biosensor-protein interactions for bioimaging applications. $^{129}$Xe NMR biosensors for carbonic anhydrase were synthesized by substituting cryptophane with $p$-benzenesulfonamide linkers of varying lengths. This motivates the development of molecular probes specific towards CA. We have shown that isozyme-specific $^{129}$Xe NMR chemical shifts clearly differentiated similarly structured CA I and II, showing one and two “bound” peaks, respectively. The appearance of two “bound” peaks
in $^{129}$Xe NMR spectra is likely due to the racemic mixture (+/-) of enantiomers. To test this hypothesis, we developed an efficient synthesis of enantiopure cryptophanes. This will also move us closer to multiplexed imaging and thus early cancer diagnostic.

32. **Self-assembly of pH dependent peptide-porphyrin nanostructures**

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Following a biomimetic approach, we synthesized polypeptides designed to induce porphyrin self-assembly into excitonically coupled nanostructures. These self-assembling aggregates are ideal candidates for incorporation into dye sensitized solar cells (DSSCs) due to their stability and favorable spectroscopic properties. Using a designed porphyrin binding motif (PBM) consisting of 3 cationic lysine amino acids, we have developed and characterized several short, amphiphilic peptides that can efficiently bind three meso-tetra (4-sulfonatophenyl) porphine (TPPS$_4$) molecules and facilitate three-dimensional orientation into an excitonically coupled J-aggregate. The ability of the peptide to act as a scaffold for TPPS interactions was shown to be dependent on the sample pH. The impact of pH on peptide secondary structure conformation and TPPS$_4$ binding was monitored using a combination of fluorescence, absorbance and circular dichroism spectroscopy. Under all conditions tested the peptide was shown to cooperatively bind three TPPS$_4$ molecules per peptide with little change in $K_d$ from pH 1.8 through 7.6. At low pH (3.6 and below) the peptide adopted a random coil conformation and allowed for the TPPS molecules to form the J-aggregate structure. Upon neutralization of the sample pH, the peptide adopts a predominantly alpha-helical structure which is concomitant with the loss of J-aggregate formation within the TPPS molecules. Using peptides that containTrp at different positions (with respect to the PBMs) initial measures of the sequence specificity of the cooperative binding event in terms of which PBM sequence is more likely to be the initial binding site.

33. **“Umpolung” molecular containers: Encapsulation of anions and small molecules**

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Molecular encapsulation phenomena have received a great deal of attention in recent years related to the unique properties and behaviors that arise in systems of intimately associated “molecules within molecules.” Synthetic, container-like nanostructures—e.g. carcerands, cryptophanes, nanocontainers, etc.—are commonly constructed from electron rich, pi-basic aromatic rings. As such, their host cavities are generally well suited for the complexation of neutral molecules and cations, but display little affinity for anionic guests. Recognizing that the appendage of electron withdrawing transition metal moieties to arenes enhances the electrophilicity of arene ring carbon atoms, a family of molecular containers has been so-modified in an attempt to yield “umpolung” or polarity-reversed capsules with ostensibly pi-acidic cavities. Observations concerning selective anion encapsulation as a function of container volume, solvent, and anion characteristics will be highlighted in the context of resurgent interest in the non-covalent anion-pi interaction. The application of water soluble forms of these capsules toward the complexation of small molecules and gases (e.g. xenon) will also be described.
34. Conformational changes in structurally well-defined β-helical peptides on adsorbing to quartz surfaces

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The aim of this study is to determine the conformational changes that occur in model hydrogen-bonded peptide secondary structures upon adsorption to model quartz surfaces. The model peptides were designed to form monomeric β helices that have been previously well-characterized in solution by NRM and electronic circular dichroism (ECD). After adsorbing the peptides from solution onto quartz slides, the slides were stacked and placed in a conventional 3 mL quartz cuvette. This experimental setup furnished sufficient ECD signal to demonstrate that the model peptides unfold to varying degrees on adsorbing to quartz. These results represent an early step toward understanding protein adsorption to surfaces—a phenomenon that underlies many deleterious processes, including biofouling and nonspecific binding in biosensors.

35. Self-assembled Nano/microwires of melamine with organic acids -- a new family of proton conductive materials

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The characterization and proton conductive applications of nano/microwires of melamine with organic acids are reported in this work. These nano/microwires are readily prepared by evaporation of water in the mixture solutions. Attenuated total reflection infrared (ATR-IR) and thermal analyses showed that the complex were held by hydrogen bonds and p-p interactions. Transmission electron microscopy (TEM) images and the electron diffraction patterns showed that the molecules in a nano/microwire were oriented with their long axis perpendicular to the wire and the n-n stacking direction parallel to the wire. The proton conductivity of one type of these nano/microwires is 4.5 S•cm-1, which is the most proton conductive organic materials reported so far. The results showed that nano/microwires of melamine with organic acids hold the promise as the most efficient proton conductive materials for fuel cell devices.

36. Smart assemblies and other adventures in supramolecular space

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The bottom-up approach to the construction of supramolecular nanostructures requires the availability of recognition motifs that are easy to synthesize and self-assemble with good selectivity and fidelity. The guanosine (G) and related derivatives stand out as excellent candidates for such purposes since they can form tetrameric structures that self-assemble in the presence of a variety of cations to form higher ordered structures known as supramolecular G-quadruplexes. Our strategy for nanoconstruction relies on the use of recognition motifs made from 8-arylguanine derivatives (8ArGs) that are relatively easy to make and offer robust and reliable self-recognition properties in both organic and aqueous media. We will show that the properties of the resulting supramolecular assemblies can be modulated by parameters that are intrinsic (i.e., structural features) or extrinsic (environmental conditions such as solvent, temperature, cation template) to the 8ArGs. The use of intrinsic parameters to drive the formation enables the reliable construction of a desired assembly with relative independence from the environmental conditions. For example, we have developed derivatives that show isostructural self-assembly in both organic and aqueous environments. Modulation of extrinsic parameters, on the other hand, enables the elaboration of responsive systems that switch their state as a function of external stimuli. We will illustrate this phenomenon with examples of solvo-,
metallo-, photo-, and thermo-responsive systems. We will highlight the versatility of these systems in the development of smart self-assembled dendrimers and self-assembled receptors.

37. Comparison of fibrillar structures and properties of hydro- and organo-gels prepared from (R)-N-alkyl-12-hydroxyoctadecylammonium chlorides, efficient ambidextrous gelators

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(R)-12-Hydroxystearic acid ((R)-HSA) and many of its amino derivatives (N-HSAM where m = 1, 2, 3, 4 and 18) are able to gelate several organic liquids.[i] Here, we report that simple conversion of the amines to their ammonium salts, N-HSAMCl (where m = 1, 2, 3, 4, 5, 6 and 18), increases significantly the range of liquids and efficiency with which they gelate. ir gelation efficient ambidextrous gelators based on ammonium chloride salts of the N-HSAM. Thus, <1 wt % of several of the homologues of the N-HSAMCl is able to gelate water as well as organic liquids. Polarizing optical micrographs show that the self-assembled fibrillar networks of the hydro- and organo-gels consist of spherulitic objects. The molecular packing arrangements of the fibrillar networks of the gelators in aqueous and toluene gels, as well as in their neat solids, will be compared. The fibrillar structures of the gels will be compared also at different length scales using data from cryo-SEM and small angle neutron scattering.

We thank the National Science Foundation for its support of this research.


38. Supramolecular Anion Binders and Transporters

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This presentation will examine recent advances from the author’s lab in the development of synthetic compounds for the binding and transmembrane transporters of anions, highlighting the underlying principles of ligand design and the promising applications of such compounds to biochemical systems.
39. Purification of Amyloid Beta specific antibodies through Surface Plasmon Resonance detection

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Amyloid Beta (Aβ) is a peptide contributing to Alzheimer’s disease (AD). Aβ plaques are thought to build up over time around dying neurons in the brain. These stable plaques are created by the clumping of Aβ from isolated monomer forms initially into oligomers and finally into insoluble fibrils known as amyloid. While the plaques are primarily comprised of amyloid fibrils exist in the plaques, the oligomeric conformers show a higher neurotoxicity than the monomeric or fibril forms. Finding a way to remove this peptide from the brain could counteract the debilitating symptoms of this disease. The compromised function of aging immune systems can prevent identification of neurotoxic Aβ oligomer or fibril forms. One proposed method of AD treatment is strengthening the AD patient’s immune system to remove the pathological forms of Aβ before they damage the brain. Bolstering the ability of the immune system to fight excess Aβ may serve as a preventive measure, or may even allow reversal of lost brain function. Therapeutic uses for Human Intravenous immunoglobulin (IvIg) are being explored in fighting a variety of diseases. Human IvIg contains a pool of antibodies from blood donors. This IvIg used directly to treat Alzheimer’s disease would have no specificity towards the Aβ peptide and could cause unwanted immune responses. Finding a way to concentrate the IvIg in anti-Aβ antibodies would lead to a more efficient and less damaging treatment for AD. The technique that was explored is Biacore Surface Plasmon Resonance to purify and enrich anti-Aβ antibodies from IvIg. This system allowed collection of anti-Aβ antibodies that show different binding affinities towards Aβ monomers and oligomers. Dissociation of weaker binding antibodies occurred at a higher rate than the higher affinity binders. These rates of association and disassociation are used to calculate the binding affinity towards Aβ. SPR collection will enrich a cocktail of anti-Aβ antibodies that can be used in testing animal models in the future. Testing was performed on three sample types to determine any specificity of IvIg. Forms of Aβ, which were bound to CMS sensor chips for detection, were monomers, native oligomers and SDS resistant oligomers. Results have shown higher binding towards oligomeric forms of Aβ. Regeneration of CMS chips was done with 0.5% SDS solution to remove bound IvIg.

40. Mutagenic effects of Silver Nano particles on bacterial DNA

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Silver (Ag) nano particles were synthesized in-house in one-step process by the reaction of silver nitrate, Tris [trimethoxysilylpropyl] isocyanurate and trioctyl amine. The nano Ag particles were then tested for toxicity on Escherichia coli ATCC # 2374. Various solvents as well as silver salts were tested for their toxicity on E. coli. Nano materials can cause cell death in bacteria by binding to cellular DNA and organelles, thus interfering with normal cell function. We are interested in studying the effect of nano Silver on bacterial DNA. After treating the bacteria with nanosilver, we extract bacterial DNA and isolate a set of standard size fragments using restriction enzymes. We then assess whether binding of nano Silver to bacterial DNA causes cell death by examining the pattern of DNA gel electrophoresis in bacteria treated with Nano Silver and those not treated with nanomaterials. This marker assay, Restriction Fragment Length Polymorphism may help assess any changes in bacterial DNA due to interaction with nanosilver. This data correlates well with cell death assayed by standard antimicrobial assays.
41. **Study of the mechanism of the binding of IHF to the DNA**

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Integration host factor (IHF) of Escherichia coli is a sequence-specific, 22KD hetero-dimeric DNA binding protein. It is member of the DNABII family and IHF is primarily known for its architectural function. It facilitates interaction between components of a nucleoprotein array by binding to the DNA in a sequence specific manner and introducing a sharp bend of >160° in the DNA bringing the flanks of the DNA closer together. The U turn helps the other proteins to bind to the DNA.

The subunits of IHF, IHFα and IHFβ, each subunit have 3 α helices and 4 β strands. The IHF binds to the DNA in a sequence specific manner but recognizes its cognate sequences with the help of structural parameters (‘indirect readout’). DNA with specific IHF binding sites and specific restriction sites is used for this purpose. The IHF binding site has 3 sub-sites, those are 5’- TATCAA-3’, which is the center region of the sub-site, and 5’-TTR-3’, where R is A or G and, the third is poly A-tract. The objective of this research is to find the dissociation constant of the IHF and the DNA by using the gel shift assay and fluorescent dyes. The dissociation constant (K\(_D\)) is the concentration of IHF at which the concentration of free DNA and bound DNA is the same. The K\(_D\) was just slightly above then the previous work by other scientists. The relative dissociation constant of different sequences and structure variants of the DNA site will be found. The other objective is to find the time constant for establishing the equilibrium using the competition between different sized IHF substrates. This would help us to better understand the interaction between the protein and the DNA and how the relative affinities of the IHF changes with the change in DNA sub sites and other variants.

42. **Enhancement of sensitivity and specificity of carbon nanotubes in diagnosis of prostate cancer based on carbon nanotube field effect transistors Comparison of The Carbon Nano Tube Field Effect Transistor direct binding assay and Enzyme Linked Immunosorbent Assay for detecting Prostate Specific Antigen.**

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We investigated a simple and sensitive method for the real-time detection of a prostate cancer marker through label-free protein biosensors based on a carbon nanotube field effect transistor (CNT-FET). The important factors for the development of effective biosensors were high sensitivity and simplification of the pretreatment Process. We were able to lower the detection limit to a protein concentration of 1.0 ng/ml, without cutting antibody or labeling the target proteins. In this study, we investigated the applicability of using CNT field effect transistor based biosensor as a diagnostic instrument in transgenic mice that are a preclinical model of human Prostate cancer.

43. **Investigation of chemical nature zinc in plants**

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Zinc is an important mineral in several enzyme pathways. Deficiency in zinc can cause many problems such as slow wound healing, hair loss, low sperm counts, and impaired immune system. Zinc is
found in the soil and absorb by plants. Humans receive zinc by consuming plants or meat of animals that graze on grass. However, amount of zinc absorption to the human body depends on the nature of zinc compound present in a plant. X-ray Absorption Near Edge Structure (XANES) is a valuable tool to probe chemical environment of a central atom. We used synchrotron x-rays from National Synchrotron Light Source (NSLS) of Brookhaven national laboratory to probe chemical environment of Zinc atoms in soil and several different vegetables using both XANES and Extended X-ray Absorption Fine Structure (EXAFS). Zinc K-edge (9659 eV) X-ray absorption data were collected in fluorescence mode. Main edge energy position of soil samples and that of spinach & mineral supplements are different from each other. This indicates slightly different chemical environments of zinc atoms in each sample. Height of main absorption edge is proportional to the amount of zinc present in the sample. Relative amount of zinc in soil will be compared with that of spinach and commercially available supplements.

44. Structure of Deletion Mutant D5 RNA of a Group II Intron Ribozyme

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Group II introns are a class of self-catalytic ribozymes as well as mobile genetic elements found within the genes of all three kingdoms of life. They catalyze their own excision from pre-mRNA. It is hypothesized that pre-mRNA splicing may have evolved from group II introns due to the similar catalytic mechanisms as well as structural similarity of the domain V substructure to the U6/U2 extended snRNA of spliceosome. The secondary structure of group II introns is characterized by six typical stem-loop structures, also called D1 to D6. The domain V (D5) is a highly conserved Mg2+ binding platform and through extensive interactions with other intron domains, arranges the catalytic core for self-splicing. D5 is arranged into two helices separated by a bulge in between, with the upper helix capped by GAAA tetraloop. The NMR titration of magnesium ions with D5 indicates that it acts as a potential metal binding platform. Here we report the structural dynamics of a deletion mutant of D5 which is defective in catalysis of the substrate, but effective in binding to D123 domain.

45. Rapid Diagnosis of E. coli using the Carbon Nano Tube Field Effect Transistor Direct Binding Assay

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ELISA, and other methods based on the same principle, are sensitive and specific, but they suffer from several disadvantages, such as their inherent complexity and requirement for multiple reagents, incubation and washing steps and require a relatively large sample size. We have adapted a new Carbon NanoTube field effect transistors (CNT-FET) based platform to capture Escherichia coli antigens using only the capture antibody showing good correlation with an established ELISA assay. Contrived positive and negative specimens were used to test the new CNT-FET platform and results were obtained within three minutes per each sample. The test is easy to perform, rapid, and cost efficient making it a valuable screening tool for E. coli.
46. Structure and Function of Selenoprotein K

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Selenoprotein K (SelK) is a membrane selenoprotein that is critical to longevity. Selenoproteins contain the genetically encoded amino acid selenocysteine that is predominantly found in enzyme active sites where it provides high chemical reactivity and specificity. The function of SelK is unknown but it was shown to participate in anti-oxidant defense in vivo, possibly in the Endoplasmic Reticulum Associated Protein Degradation (ERAD) pathway.

To facilitate SelK structural and biophysical characterization, we have developed bacterial overexpression strategy using a fusion partner to stabilize and solubilize SelK. The fusion protein can be cleaved from SelK in the presence of a variety of different detergents compatible with structural characterization by nuclear magnetic resonance spectroscopy. Furthermore, we demonstrate the incorporation of selenium in SelK forming the functional selenoprotein.

47. Ribosomal protein L2: Transmitting information to peptidyltransferase center.

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Successful synthesis of cellular proteins relies on the proper functioning of the ribosome, a large ribonucleoprotein complex, composed of 4 ribosomal RNAs (rRNAs), and approximately 80 intrinsic proteins. There are numerous biochemical interactions between these rRNA and protein chains; the two ribosomal subunits must communicate efficiently to carry out multiple steps that occur during polypeptide biosynthesis. The aim of this study is to investigate the role of ribosomal protein L2 (L2) using the model organism baker’s yeast, Saccharomyces cerevisiae. L2 is a large subunit protein which is essential for viability and is highly conserved throughout all three domains of life. We have chosen to focus on two important regions of L2: 1) an internal loop of L2 ("L2 loop"), which extends into the peptidyltransferase center of the large subunit; and 2) the "inter-subunit region" that participates in forming the B7a/b intersubunit bridge by interacting with the small subunit rRNA. Examination of numerous ribosome structures reveals that this interaction is highly conserved. We have mutagenized the loop region amino-acids to those spanning the full range of biochemical properties. Small stretches of important amino acids in the bridge region were substituted with alanines for charge and size reduction. Genetic and functional analyses of the mutants have suggested some important candidates for deeper study. Biochemical analysis, including ligand (tRNAs, elongation factors) binding and rate of peptide bond formation, and the structure probing method SHAPE(selective 2'-hydroxyl acylation and primer extension) are being used to understand the influence of these mutants on ribosome function. Defects in fundamental processes such as translation can be the underlying cause in many complex pathologies, including Diamond Blackfan Anemia. Therefore it is crucial to understand the role of L2 in the ribosome.
48. **Synthesis and characterization of dialkylphosphate ionic liquids**

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Ionic liquids (ILs) are salts that melt below 100 °C. They are generally recyclable, have a wide liquid range, low vapor pressure, high conductivity, and high thermal stability. As a result of these properties, ILs have applications in diverse areas including use as alternative solvents in chemical reactions and as custom solvents for dissolving polymers. It’s crucial to understand and eventually be able to predict the physical properties of ILs in order to tailor them for specific applications. This project concentrates on the synthesis and characterization of a series of ILs bearing functionalized imidazolium and pyrrolidinium cations and alkylphosphate anions. The ILs were prepared by reacting the amines N-methylpyrrolidine or 1-methylimidazole with an alkylhalide containing the desired functional group. The halide anion in the resultant salt was then exchanged for the dibutylphosphate anion. The diethyl- and dimethyl phosphate ILs were prepared by direct reaction of the amines with the corresponding trialkylphosphates. $^{13}$C, $^1$H and $^{31}$P Nuclear Magnetic Resonance spectroscopy was used to verify the structures. The ILs were characterized for their physical properties including viscosity, conductivity, density, and thermal profile. Preliminary Thermogravimetric Analysis (TGA) results show that most of the ILs are thermally stable up to 240 °C and thus are more suitable for high temperature applications than many conventional solvents.

49. **The effect of branched alkyl chains on the dynamical properties of ionic liquids**

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Ionic liquids (ILs) are salts which are characterized by having low melting points (under 100 °C), and are generally made up of a large organic cation and a relatively small inorganic anion. Possible applications for ILs include alternative solvents, battery electrolytes, waste recycling and solar energy media. In order to know which IL can be tailored to a specific task, the dynamical properties of such ILs need to be investigated. This fundamental investigation focuses on synthesizing ILs containing imidazolium and pyrrolidinium cations bearing linear and branched alkyl chains of the same length. The ILs were synthesized by reacting an amine with an alkyl halide to generate the halide salt. The halide salt was converted to bis(trifluoromethylsulfonyl)imide [(CF$_3$SO$_2$)$_2$N$^-$] IL by a metathesis reaction. The physical properties investigated include the thermal profile (melting point and glass transition), viscosity, conductivity, and density. Differential Scanning Calorimetry (DSC) experiments were carried out to determine the thermal profile. The viscosity was measured using a viscometer. Conductivity and density were performed using standard methods for IL characterization. Preliminary conductivity, DSC, viscosity, and density results revealed that ILs bearing branched alkyl chains have lower conductivity, density, and melting points, but higher viscosity than their linear chain analogues. The physical property data obtained suggests that branching in alkyl chain substituents do have an effect on the physical properties of ionic liquids. Future work will focus on completing the characterization of similar compounds in order to assess the effect of branching more effectively.
50. Does cold exist?

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Using a programmable modeling environment called NetLogo, I designed an activity which allows high school chemistry students to explore temperature variation as a manifestation of kinetic energy of atoms or molecules. Students observe and manipulate the temperature of materials in this virtual environment. The goal is for students to realize that absolute zero exists as zero kinetic energy and that cold is the absence of heat and kinetic energy, while heat is not the absence of cold.

51. Using Flash movies to envision ionic compound formation

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Electrostatic bonds are initiated by electron exchanges. Atoms (or complex ions) that have loosely bound electrons donate the electrons to other atoms that need to fill the outer shell. The product of electrostatic attraction between cations and anions is an ionic compound. I have created Flash animations to aid high school chemistry students’ in visualizing ionic bond formation. The objective of these animations is for students to envision the formation of ionic compounds by electrostatic bonds using familiar symbols, which are expressed as jigsaw puzzle pieces. The symbol of an atom with loosely bound electrons is a puzzle piece with an ‘outie,’ and an atom with empty spaces in the outermost shell as a puzzle piece with an ‘innie.’ The animations are ionic compound 1+ to 1-, 1+ to 2-, 1+ to 3-, 2+ to 1-, 2+ to 2-, 2+ to 3-, 3+ to 1-, 3+ to 2- and 3+ to 3-.

52. Identifying genes in mycobacteriophages genome

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Mycobacteriophages have the ability to infect bacteria harmful to eukaryotes, prokaryotes, and archaea alike. There are about 1031 bacteriophages in the biosphere, with each bacteria species having a minimum of 10 phages infecting it. Technological advances to decipher the genomes of virulent phages have allowed us to browse through the genome of mycobacteriophage Eric B. The Workflow tools designed by Howard Hughes Medical Institute provide easy access to standard bioinformatic tools needed to identify key components of the mycobacteriophage genome such as transferRNA, Shine Delgarno Scores, Coding Potentials, and protein query comparison across their Biomedical Database. Specific programs include: Aragon and tRNAscan-SE, SD Finder, GeneMark TB, GeneMark, Glimmer, and BlastX. Apollo and GeneBrowse allows us to display the area of our DNA Sequence to identify its components as putative protein-coding genes and the HHMI SEA give us a portal to compare results with students across the nation.

53. Using flash technology to assist high school students’ visualization of atmospheric gases

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While working with high school students, I observed a lack of students’ understanding of gases in the Earth’s atmosphere. While it is true that students have an idea about the air being present in the atmosphere, they do not understand relative proportion and structures of these gases. When asked, “What is the most abundant gas in the atmosphere?” The most common response is that oxygen is the most abundant gas. I believe that this is a common response, because teachers tend to
over-emphasize the importance of this gas for human survival and fail to discuss other gases, such as nitrogen. In addition, students also lack understanding of the structure of atmospheric gases. To address these concerns, I created an Adobe Flash animation and embedded it in a PowerPoint presentation on layers of the atmosphere, which highlights the structure of the gas molecules and the concentration of gases within the layers of the atmosphere.

54. **Thermal property of Fe nanoparticles embedded in porous glass medium.**

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Thermal property is an important mechanical engineering issue. The advances in nanotechnology enable novel composite materials for new applications. This project aims to develop a numerical computational tool at the undergraduate level that would provide solutions as guidance feedback to the laboratory fabrication process as well as to characterize the property of the end products. The material model used in the project is Fe nano-particles embedded inside a porous glass medium. Steady state boundary conditions were simulated. Heat transfer of nanoparticle doped porous glass substrate was studied using a two-dimension heat transfer model and the associated differential equations were solved numerically. The spatial distribution of the embedded nanoparticles was modeled as a simple Gaussian spatial distribution. The results reveal that thermal gradient across the medium exhibits non-Gaussian behavior and the temporal development to be a strong function of the boundary temperature.

55. **Co-polymerization of partially sulfonated polyaniline nanofibers for electrostatic interaction with gold nanoparticles**

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Nanocomposites of polyaniline nanofibers and gold nanoparticles (NPs) are of interest for catalysis, sensors, light-harvesting, and organic electronics. In light of their many applications, specific and reliable loading of Au-NPs onto nanofibers is desirable. Towards this, we have explored an electrostatic interaction between these two materials by combining sulfonated nanofibers, which are negatively charged, with positively charged Au-NPs. The charge on the NPs arises from the stabilizing shell that controls the size and prevents aggregation. The deposition of positive Au-NPs onto the nanofibers is generally greater than for negative Au-NPs, which appear to be repelled from the negatively charged polymer. However, sulfonation also significantly increases the solubility of the polymer in aqueous solution, often resulting in partial to full loss of the nanostructure. To balance the desired electrostatic effect against the unwanted solubility, we have copolymerized varying mole ratios of aniline and 2-aniline sulfonic acid, facilitated by addition of an initiator (N-phenyl-1,4-phenylenediamine), to obtain partially sulfonated nanofibers. Although we do not yet know the actual degree of sulfonation of the co-polymers, FTIR confirms the presence of sulfonic acid groups and SEM reveals changes in morphology with the monomer ratio and amount of initiator. Initial results indicate greater deposition of positive NPs with increasing sulfonation, but also increasingly fused nanofibers above 50% sulfonation.

56. **Kaltura as a tool for teaching organic chemistry**

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Kaltura is a tool by which students can create and post short videos to the web. This paper discusses a number of problems presented to students using molecular models. The problems given to the
students involve standard concepts in organic chemistry concerning geometric issues with molecules or organic reactions. The use of Kaltura allows for a quick and simple method for determining a student's basic understanding of standard concepts in organic chemistry. A number of non-graded student exercises are described in this paper. In addition, the use of Kaltura in an examination environment is also described. Typical student postings to the problems, via Kaltura, are discussed.

57. An experiment to display the concept of limiting reactants using an iron (III) salicylate complex by utilizing a PASCO colorimeter

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The determination of the amount of aspirin in a commercial aspirin sample is a "classic" freshman laboratory exercise using a Spectronic 20 spectrophotometer. PASCO has a version of this experiment using an Ocean Optics spectrophotometer coupled to their hardware. We describe a version of the "aspirin" experiment, showing student data, utilizing the cheaper PASCO colorimeter. We also describe an adaptation of the experiment to determine the concentration of ferric ions in solution utilizing the same PASCO colorimeter.

58. Examination of mtDNA gene sequence (cytochrome b) to show the evolutionary relationships between regional populations of the brown howler monkey (Alouatta guariba) in the atlantic coastal forest of Brazil.

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We analyzed mtDNA sequences of the cytochrome-b gene from brown howler monkeys living in the Atlantic Coastal forest in Brazil. Our samples derive from populations from three different localities: Rio de Janeiro state in the north, Santa Catarina state in the south and São Paulo state that lies in an intermediate geographic position. We used maximum parsimony and neighbor joining methods to analyze the cytochrome b genetic variation to make inferences about the intraspecific genealogical relationships of howler monkeys from these three populations. Our findings indicate that cytochrome b gene variation is structured into two main clades. Among the three populations, the cytochrome b sequences from Santa Catarina and Rio de Janeiro each form separate clades, with no shared diversity. However, the sequences from monkeys from São Paulo are represented in both of these clades. We hypothesize that the Santa Catarina and Rio de Janeiro populations underwent a forced separation related to fragmentation of the Atlantic Forest perhaps during the Pleistocene Epoch as has been hypothesized for other species. We also hypothesize that the São Paulo population formed at a subsequent time following environmental change and forest restoration, thereby accounting for its shared variation with both northern and southern populations.

59. Falcon-rodent predation: An introduction to the scientific method

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This NetLogo simulation is a result of a drop in the falcon population in Horicon Marsh state park, Wisconsin. I have modified the wolf-sheep predation to fit falcon, rodent and marsh vegetation as an ecological chain. Students are asked to vary one of nine variables, make a prediction of resulting falcon and rodent populations. They then run the software and analyze the results. Doing this repeatedly allows students to understand the scientific method.
60. Synthesis of protected oxyallyl silane derivatives for use as homoenolate equivalents

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New methodology is proposed in which oxyallyl silanes will act as an oxidized allyl silane equivalent in the addition to electrophiles. In this way, the oxyallyl silane will function as a homoenolate equivalent by attack through the terminal alkene carbon. The resulting addition products contain a synthetically useful vinyl ether functional group that serves as an oxidized alkene or aldehyde. This circumvents the need to functionalize the alkene, which can often be difficult when the alkene is near a sterically hindered position or if the compound contains a nitrogen. The preparation of derivatives of oxyallyl silanes (shown below) will be described where the protecting group on the oxygen is modified. Future work will involve the assessment of the electronic and steric properties of the resulting oxyallyl silanes and their ability to undergo an oxidative addition to a variety of electrophiles, such as phenols and vinylogous amides.

61. Development of oxyallyl silanes as homoenolate equivalents in the oxidative addition to substituted phenols

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New methodology is proposed in which oxyallyl silanes will act as an oxidized allyl silane equivalent in the addition to electrophiles. In this way, the oxyallyl silane will function as a homoenolate equivalent by attack through the terminal alkene carbon. One demonstration of this method is the oxidative addition to substituted phenols. The oxyallyl silane will add to either the ortho or para position of the phenol. The regioselectivity of addition will be determined using a variety of substituents on the phenol and by screening the reaction conditions, including the oxidant, solvent, and temperature. The resulting addition products contain a synthetically useful vinyl ether functional group that serves as an oxidized alkene which is at the aldehyde oxidation state. The utility of the method will be presented by converting the products to small, complex ring systems that are often found in natural products. The initial stages of this work and the feasibility of the reaction will be presented here.
62. Nitration of methyl benzoate - an extension of an old experiment

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Organic textbooks often state that o-, p- and m- directing groups on a benzene ring do not give these isomers exclusively. However, in a popular lab experiment on nitration of methyl benzoate students are told to discard the methanol used to recrystallize their product, methyl 3-nitrobenzoate (I) in the appropriate waste container [Org Syntheses Coll Vol 1, 372 (1941). If instead they evaporate these washings to dryness, the presence of methyl 2- (II) and methyl 4-nitrobenzoate (III) can be established experimentally by 1H nmr. While there is some overlap of peaks, each isomer has a unique 1H signal which can be integrated to quantitate it without prior physical separation of isomers. These are 8.8 ppm for I, 7.9 ppm for II and 8.3 ppm for III. GC-MS has been recommended for the separation and quantitation of the product without isolating it [J Chem Educ 84, 1679 (2007)]. TLC also has been reported for this analysis, although it was noted that III [2% yield] could not be detected [J Chem Educ 85, 1623 (2008)]. We prefer to keep the isolation and characterization of I by mp [75-77°C] and add the 1H nmr analysis of I, II and III. 13C nmr also may be used to measure the products, especially if the DEPT90 program, which detects only CHs, is used to simplify the spectrum. Supported in part by a Fordham University Faculty Research Grant and by an NSF grant for a 300 MHZ nmr spectrometer.

63. Gemstone Team ONLINE: How the presence of an audience affects teacher immediacy behaviors in online introductory Chemistry lectures

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Online education is a viable option for administering college level classes and is becoming a relevant issue as class sizes grow and instructors need to reach a broader audience. Many question whether students can learn effectively in an online class as opposed to in a traditional lecture hall class; however, current research provides contradictory results. Team ONLINE will quantify student success, teacher immediacy, and perceived learning levels among three lecture formats: a traditional classroom, an online video with a live audience, and an online video without a live audience. In our experimental case study in a Chemistry class, students will be randomly assigned to one of these three conditions, exposed to course material, then measured for success by an objective posttest and for perceived learning and teacher immediacy through a subjective survey. We expect to find a significant difference in perceived learning and teacher immediacy among the three groups due to varying levels of teacher immediacy.

64. Successful Implementation of Project-Based Biochemistry Laboratory Curriculum at West Chester University of PA

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Biochemistry Laboratory (CRL476) Curriculum Revision was a two year project (2008-2010) that was funded by NSF-CCLI program (Award # 0737266). The revised course was implemented successfully and the PI plans to continue the revised curriculum to teach the biochemical principles and techniques using this innovative approach. The two phase approach worked well in the context of knowledge and skill acquisition in phase I and application of the acquired skills in phase II through students' independent projects. Examples of selected independent projects will be shared in the presentation.
Student learning assessment results were, as one might expect, somewhat mixed. In some cases, our assessments clearly supported our belief that students were learning biochemical concepts, developing an understanding of the scientific approach, and engaging in creative and critical thinking throughout the laboratory course. In other cases, results were less clear. Detailed assessment results will be provided (by semester) for each measure associated with each student performance goal we set in advance (both in general and by student learning outcome). We have also made recommendations for future implementations of the project-based laboratory course in biochemistry.

65. Extraction and analysis of lavender oil from Pennsylvania-grown *Lavendula augustifolia* for use in fragrances

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The production of compounds that make up a fragrance is highly dependent on the environment in which the plant or animal is grown. Pennsylvania-grown lavender has not been studied for molecular content of its essential oil. Essential oil of lavender was extracted from locally grown lavender plants, using steam distillation or alcohol extraction, from plant tissue samples collected mid-winter and mid-spring. Analyses by gas chromatography was employed to determine the volatile compounds content and distribution. Results were compared to commercially available lavender extracts.

66. Inhibition of thrombin-catalyzed fibrin clot formation by the tetrapeptides LSPR and ISPR

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Thrombin, the central enzyme in the clotting cascade, is the target for investigation into anti-hemostatic drugs. Two tetrapeptide models, ISPR and LSPR, were studied for inhibition of clot formation by spectrophotometric clot opacity measurements. Results presented here indicate that ISPR and LSPR initially inhibit clot formation; however, the final clot is more opaque than a clot formed without added inhibitor. Uninhibited clot formation results in a hyperbolic plot of absorbance versus time. The sigmoidal shape of the plot for clot formation in the presence of ISPR or LSPR indicates a cooperative binding mode for the tetrapeptide, fibrinogen, and thrombin.

67. Investigating the chemical interactions between SWNTs and oxides of hafnium

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SWNTs, as well as, hafnium oxide have demonstrated potential electronic applications due to their unique properties. In this study we investigated the chemical interactions of hafnium t-butoxide with single-walled carbon nanotubes (SWNTs), which were initially functionalized with hydroxyl groups. Several techniques were investigated to obtain SWNTs with multiple hydroxyl functionalities without destroying the structure of the nanotubes. The resulting hydroxyl functionalized SWNTs were reacted with hafnium t-butoxide and the resulting adduct was studied by microscopic and spectroscopic techniques. The functionalized samples were analyzed by FT-IR and UV-Vis spectroscopy and by TEM microscopy.
68. Formation of porous micron-scale spheres of poly(o-toluidine)

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For decades, the oxidative polymerization of polyaniline and its ring-substituted derivatives was known to produce only irregularly structured materials. However, new methods are now known by which nanoscale fibers are easily prepared in high yields. Because properties such as solubility or conductivity may be tuned via ring-substitution, these high surface area nanomaterials are broadly applicable in sensors and other electronic devices. In our own investigations of poly(o-toluidine), the methyl-substituted analog of polyaniline, we have produced highly porous micron-scale spheres. Scanning electron microscopy has revealed that this is not the native morphology of the polymer. Rather, it is formed during the post-synthetic workup when the crude product, obtained as a thick precipitate dispersed in aqueous acidic solution, rapidly agglomerates upon addition of ammonium hydroxide. This is not observed if the precipitate dispersion is made neutral before the base is added. Generally, the yield of porous spheres is better when the precipitate is highly concentrated, though they are typically fused and/or damaged. If the concentration of the precipitate is reduced, either by diluting the crude product with water or simply by using lower reactant concentrations, only unstructured material is obtained. We therefore hypothesize that porous spheres are formed by an intermolecular interaction that depends on the particle density. However, a chemical process (i.e. polymer cross-linking) is unlikely, as identical FTIR and UV-Vis spectra for both morphologies indicate they have the same composition. In other words, no new bonds accompany sphere formation. By slightly diluting the crude mixture prior to addition of the base, discrete and undamaged spheres have been obtained, perhaps by reducing the extent of the interaction. Reproducibility has been a challenge, however, thus our focus is on determining the nature of the interaction and the best conditions for producing spheres. Notably, we have found that once these structures are formed, they are stable in acidic and basic environments from pH 1 to 10. We hope to use this novel porous material as an encapsulant for other smaller particles.

69. Teaching the POGIL way: Perspective of a teaching assistant (TA)

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POGIL (Process Oriented Guided Inquiry Learning) is a method of teaching in which students work together in a group on an ‘activity’ in the classroom. These activities are comprised of a guided inquiry in which key questions explore the central idea in a model and exercise, problems that integrate previous concepts. In this system the students teach themselves and each other. Typically, they work four in a group with well-defined roles. Within the framework of the class they exchange ideas and try to solve problems.

At Stony Brook University, one POGIL class supplements three weekly lectures. TA’s facilitation of the activities plays an important role in filling the gaps in the knowledge gained from these lectures. Small POGIL classes ensure individual attention to students – both strong and weak. The POGIL way enables the students, who have a grasp over the subject material, to convey it to the weaker participants. But it is not always possible for one student to help another. At this point the TA comes into the picture. TA facilitates not only the achievement of correct answers, but also smooth functioning of the groups with equal participation from all the students.

A tremendously important job during these POGIL classes is to instill confidence among students regarding the subject material. The feeling of “I can also do it” is very important for student psyche to perform well in the tests. To help students gain that mental confidence, the student should be
helped to figure out the problem, instead of directly given the answer. Presenting questions to them and asking them to write or draw a physical picture often solves the problem.

The poster will summarize the role a TA plays to facilitate achieving the maximum benefit for the students.

**Medicinal Chemistry Poster Session I**
Organizer: P. Deshong

**70. Nitric oxide-releasing materials for wound healing and surgical applications**

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Wound healing is a complex process which can be adversely affected by a wide variety of factors including, for example, infectious agents and diabetes. Wound dressings which release nitric oxide (NO) have the potential to stimulate healing because NO has antibacterial properties,\(^{1}\) promotes angiogenesis,\(^{2}\) and promotes collagen synthesis.\(^{3}\) Reduced endogenous synthesis of NO has been implicated in diabetes-impaired wound healing.\(^{4}\) We will describe the preparation of polymers containing the NO-releasing diazeniumdiolate functional group (–N=NO\(\rightarrow\)) \(^{(1)}\), both covalently bonded to the polymer as well as in the form of blends with the small molecule NO carrier PROLI/NO, which may serve as new active wound dressings. Polymers which have been converted into NO-releasing form include a polyurethane, polyacrylonitrile, nitrile rubber, styrene-acrylonitrile (SAN) resin, cotton fabric, and “Nu-Knit” surgical hemostat. The methods used will be described, including the new chemistry developed which involves the formation and subsequent base-induced reaction with NO of sites containing one or more acidic hydrogens to form novel carbon-bound diazeniumdiolates. Application to small molecule analogs of these polymers will also be described. Funded by NCI Contract HHSN262200800001E and by the Intramural Research Program of the NIH, National Cancer Institute, Center for Cancer Research.

**References:**


**71. Electrospinning crosslinked chitosan fibers. Part I: Chemical analysis**

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Chitin is the second most abundant, naturally-occurring polysaccharide. The deacetylated co-polymer of chitin, chitosan, has both \(N\)-acetylglucosamine and glucosamine units depending on the degree of deacetylation. Due to its increase solubility over chitin, chitosan (CS) has potential applications in the medical field. Crosslinking improves the chemical and mechanical stability of electrospun chitosan fibers. In this study, a novel method of crosslinking was performed using genipin, hexamethylene-1,6-di(aminocarboxysulfonate) (HDACS) and epichlorohydrin (ECH). Morphological and structural tests were conducted using field emission scanning electron microscopy (FESEM) and Fourier transform infrared (FTIR), respectively.
Chemical stability tests were also performed to determine the stability of the mats in acidic, neutral and basic solutions after 15min and 72h immersion. FESEM micrographs revealed that crosslinked CS could be electrospun with genipin, HDACS and ECH. Mean fiber diameters were 267±199nm, 644±359nm and 896±435nm for genipin, HDACS and ECH-crosslinked mats, respectively. Heat and base activation of CS-HDACS and CS-ECH crosslinked mats decreased the mean fiber diameters. Moreover, post-activation crosslinked electrospun CS mats have improved chemical stability in 1M acetic acid (AA), water and 1M NaOH even after 72h. Tensile testing of the electrospun CS mats revealed that the crosslinkers significantly affect the fiber diameter as well as the mechanical properties.

72. Identification of new topoisomerase type II inhibitors for the treatment of multi-drug resistance Staphylococcus aureus through computer-aided drug design

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Methicillin-resistant Staphylococcus aureus (MRSA) infections have increased in hospital and community settings. They are involved in skin cellulites, bacteremia, endocarditis, osteomyelitis, and septic shock. We are applying computer-aided drug design (CADD) tools to identify new lead compounds expected to inhibit ATP hydrolysis at the ATP-binding sites of gyrase (GyrB) and topoisomerase IV (ParE). We have used Shape Signatures, a novel computational method developed in our laboratory, to scan a large chemical library of readily available compounds (the ZINC database) for molecules similar in shape to known inhibitors. Top hits from this initial scan were further validated by molecular docking using the GOLD and GLIDE docking tools. The docking results were further validated with molecular dynamics simulations to refine and rationalize predicted variations in binding affinity. A selection of the compounds predicted to be most active through in silico methods were acquired and tested for activity by determining their minimal inhibitory concentrations against MRSA strain ATCC33592, with Novobiocin as a positive control.

73. Novel CXCR4/CCR2 dual-targeted fusion inhibitors

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The chemokine receptors CCR5 and CXCR4 have been shown to act as co-receptors that are required for cellular entry by the human immunodeficiency virus (HIV-1). There has been success with CCR5 antagonists being used as HIV fusion inhibitors, while CXCR4 antagonists have failed due to side effects. However, there are no such reports for the CXCR4/CCR2 dual-targeting fusion inhibitors. These two receptors co-exist as a hetero-oligomeric complex at the surface of T cells and monocytes. Because the antagonisms of CCR2 lead to the cross-inhibition of other receptors, we expect that the dual-receptor targeted antagonists would lead to the effective inhibition of HIV fusion regulated by the CXCR4 co-receptor. We employ modern docking approaches in combination with novel statistical scoring functions developed in our laboratory for structure-based virtual screening (VS). The newly solved crystal structures of the human CXCR4 chemokine receptor is utilized to dock against the unique collection of over 17.5 million commercially available compounds. We also build the structural models of the CCR2 receptor as well as the CC chemokine receptors (CXC chemokine receptors (CXCR1-CXCR7) and CC chemokine receptors (CCR1-CCR11) for cross-docking studies. In the end a total of fifteen putative hits are identified and submitted to the Psychactive Drug Screening Program and the Virology Core Laboratory of DC D-CFAR for \textit{in vitro} and antiviral activities evaluation. Our structure-based strategy has
been proved to be effective so far to achieve the goal of identification of innovative, dual-targeting fusion inhibitors.

74. The Synthesis of Heterocyclic Aryl Sulfones and the Investigation of their Potential Therapeutic Uses

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Sulfones are a class of compounds that have been shown to have activity against a wide variety of diseases. Diseases that have been treated by these types of compounds include malaria, tuberculosis, leprosy and HIV thereby making these compounds highly desirable lead molecules for research. This laboratory investigated the preparation of a group of amino aryl sulfones through an acid catalyzed reaction that rearranges a sulfonanilide to a sulfone. This synthesis method provided an easy and quick access to sulfone products. Heterocyclic sulfones of tetrahydroquinoline, indoline, and tetrahydrobenzazepine have been successfully made through this route. Tetrahydroquinoline sulfones have shown inhibitory activity towards HIV as a Non-Nucleoside Reverse Transcriptase Inhibitor (NNRTI). Structurally similar compounds, indoline and tetrahydrobenzazepine sulfones, have been synthesized for the purpose of finding similar activity as NNRTIs. While indoline sulfone analogs such as indolyl aryl sulfones have been active NNRTIs, analogs of tetrahydrobenzazepine sulfones have been published as antipsychotic agents. These aryl dicyclic compounds are examples of the diverse therapeutic uses these sulfones possess. Therefore, analogs of indoline and tetrahydrobenzazepine sulfones such as carbazole and imidobibenzyl sulfones, respectively, will be synthesized and investigated for their medicinal value. Carbazole and imidobibenzyl differ from indoline and tetrahydrobenzazepine by the addition of another benzo-fused ring to the saturated amine ring.

A computational portion of this project has identified these tricyclic sulfone compounds as potential anti-bacterial, anti-tumor, and anti-pain (analgesic) agents. The Shape Signature program compares proposed molecules to a database of ligands of known therapeutic activities based on their molecular shape. This type of comparison allows the discovery of new candidate molecule leads for ligands that are based on shape instead of traditionally by structural likeness. Subsequently, this novel method also identifies potential new drug targets for lead compounds from the compared ligands. Docking simulations of lead compounds to their potential drug targets will eliminate or confirm targets identified by Shape Signature. The use of a molecular modeling program, Molecular Operating Environments (MOE) and docking programs such as GOLD and/or GLIDE will elucidate any potential ligand-receptor interactions.

This presentation will involve the initial synthesis of carbazole and imidobibenzyl sulfone and the discovery of new drug targets by Shape Signature. Future work will explore the scope of these new targets with respect to derivatives identified to show greatest activity by the docking simulations. This portion will evaluate synthesized derivatives by means of assay screening to confirm and validate the computational portion of the project.

75. Binding of hydrophobic side chains in the S2’ pocket of Thermolysin: Is it entropic or enthalpic driven binding?

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The entropy-driven hydrophobic effect is one of the major driving forces for ligand-macromolecule binding. The binding thermodynamic parameters, and affinity, of a series of thermolysin phosphonamide inhibitors were evaluated wherein a range of hydrophobic side chains were present for interacting
with the S2’ pocket. The results showed that favorable entropy changes dominate binding when the ligand hydrophobic groups are large (e.g. isobutyl and benzyl) but favorable enthalpy dominates when the hydrophobic side chains are small (e.g. Me and Et). The cause of this enthalpy-driven binding is attributed to the formation of stronger H-bonds among the water molecules hydrating the unburied portion of the smaller hydrophobic groups in the ligand-enzyme complex. The reinforcement of the H-bond networks by the polar and H-bonding groups in the ligand-enzyme complex might be the cause of the enhanced H-bonding strength among the nearby water molecules.

76. **Potent anti-cancer activity of heterocyclic compounds with imidazo[4,5-e][1,3]diazepine backbone structure**

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Potent broad spectrum anticancer activities in vitro with no apparent toxicity of a ring-expanded nucleoside 4,6-diamino-8-imino-8H-1-ß-D-ribofuranosyl imidazo[4,5-e][1,3]diazepine (1) has been observed. Further structure-activity relationship(SAR) studies revealed that even without the sugar moiety, the heterocyclic aglycon of this nucleoside exhibit potent in vitro anti-cancer activity against prostate, breast, ovarian and lung cancers. Biological activities was tested against a series of heterocyclic compounds containing imidazo[4,5-e][1,3] diazepine ring system synthesized in our lab with different substitutions at position 1, 2 and 6-amino position. Synthesis and anticancer activities of the title compounds will be presented.

77. **Modulation of the macrophage immune response using gold nanoparticles bearing tumor-associated carbohydrate antigens**

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Macrophages are among the many specialized cells of the innate immune system that are responsible for several functions, including the release of chemical mediators, called cytokines. The levels of these cytokines can provide critical information about specific localized immune responses. Macrophages are thus attractive immune cells for studying responses against a myriad of antigens. We have been studying various methods to develop vaccine constructs containing specific structures related to tumor-associated carbohydrate antigens (TACA). TACAs are sugar moieties resulting from the aberrant glycosylation of cell surface proteins. TACAs O-linked to serine or threonine are invariably found on a family of cell surface proteins called mucins, which are heavily O-glycosylated with aberrant glycans. Two common TACAs, namely the Tn antigen (α-D-GalNAc) and the Thomsen-Friedenreich (TF, Gal-β(1→3)-α-D-GalNAc) disaccharide, have been the basis of many anticancer immunotherapeutic studies. These previous studies utilized constructs bearing multiple copies of
TACAs that are conjugated to a scaffold, such as a protein, to improve the therapeutic efficacy. This is because presentation of carbohydrates in a multivalent fashion enhances their affinity towards proteins or receptors, and thereby inducing a stronger biological response. In this work, we attached the TF disaccharides at various threonine and serine positions of a thiol-functionalized 16-mer peptide repeating unit from a specific tumor-associated mucin (MUC4) and conjugated them to a multivalent scaffold, gold nanoparticle (AuNP), of different core sizes. Bone marrow-derived mouse macrophages were treated with the AuNP-conjugates, and their cytokine profiles after 24h were determined using the cytometric bead array assay. Results indicated that for cells treated with smaller AuNPs (3-5 nm), an increase in TNF-α production was observed, especially in the case of AuNPs bearing simply the MUC4 peptide or one specific glycopeptide with the TF antigen attached to the fifth serine residue of the peptide. Interestingly, changing the position of the TF to the sixth residue decreased TNF-α production. This implies that the placement of TACA on the backbone is crucial to the response. Changing the core size of the AuNPs also had a dramatic effect on TNF-α levels. Larger AuNPs (16-40 nm) strongly increased TNF-α levels with respect to smaller AuNPs (3-5 nm). However, the increase was not specific for any particular placement of the TF antigen. Experiments with macrophages lacking most all toll-like receptors (TLRs) via knockout of the MyD88 adapter protein, showed a significant decrease in the levels of all cytokines produced, relative to wild type cells. This indicates that the AuNPs are perhaps primarily recognized by the TLRs on the macrophages. This study provides some insight into the modulation of the cytokine levels of one type of antigen presenting cell by glycopeptide-coated AuNP. This assay may help to “prescreen” specific nanoparticle vaccines for potential anti-tumor effects in vivo.

Organic Chemistry Poster Session I
Organizer: P. Deshong

78. Synthesis and Characterization of C8 Analogs of c-di-GMP
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c-di-GMP is an important bacterial second messenger that is critical for the transition between a biofilm-protected sessile state and a virulent, single cellular motile state in species like V. Cholerae and S. Typhimurium. The synthesis and solution phase structural analysis of a family of C8-modified analogs is described. Starting from unmodified c-di-GMP, elaboration at the C8 position of both guanine moieties of c-di-GMP resulted in the bromo, thio, methylthio, phenyl, and meta-acetylphenyl analogs.

Biophysical studies of all five compounds was performed using 1D and (1H, 31P, 13C) and 2D (DOSY, HMBC/HMQC) NMR to ascertain the level of G-quadruplex formation. It was found that only c-di-Br-GMP as the K+ salt form adopts the formation of higher order complexes containing guanine quartet structures. All analogs have an NMR-visible amino resonance that is most prominent at low temperatures due to protection from exchange by the self-stacking, and that disappears at elevated temperatures. This phenomena does not occur with the 8-bromo-GMP monomer, which illustrates the special structural characteristics of the C8 analogs of c-di-GMP.

79. A novel, unusual acid catalysed route to substituted 1,2-dihydropyridine via double decarboxylation
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3,4,5-trisubstituted 1,4-dihydropyridine systems are part of calcium channel blocker cardiovascular drugs, fluorescent dyes and other important molecules. We describe a simple and high yield route to these highly useful 3,4,5-trisubstituted 1,4-dihydropyridine systems via an interesting intermo-
molecular condensation and double decarboxylation. We also suggest a plausible mechanism for this interesting reaction.

80. Control of selectivity in the generation and reactions of oxonium ylides

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The synthesis of oxabicyclo[4.2.1] compounds was achieved via the oxonium ylide intermediate 2 formed through dinitrogen extrusion of the diazoacetoacetate substituted tetrahydro-4-pyranones 1. Catalytic ylide formation and rearrangement results in a mixture of two diastereoisomers formed in high yield, but with negligible dependence on either para substituents on the aromatic ring or on the catalyst that is employed. However, the use of a bulky aryl substituent resulted in the formation of one diastereoisomer. These results will be presented and discussed.

81. Highly effective one-pot approach to functionalized seven-membered 4,5-dihydrooxepins

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Seven-membered oxacycles are common ring motifs found in many pharmaceutical and biological interesting natural compounds. Representative examples range from the oxepane (Zoapatanol) to benzo[b]oxepane (Heliannuol D), and symmetrical fused ploycyclic oxepins (Aranotin). Unlike methods for the synthesis of five- and six-membered oxacycles, the synthetic strategies toward functionalized seven-membered oxacycles, especially the 4,5-dihydrooxepins, are not well documented.

Our group has a long history of using diazoacetate chemistry, and one of our interests is the heterocyclization of vinyldiazoacetates with aldehydes or imines via dirhodium(II) catalysis to form seven-membered ring heterocyclic compounds (Scheme 2, compound 5 and 6). The Davies group has reported the use of siloxyvinylDiazoacetate (1b) for the construction of seven-membered carbocycles (7); this reaction shows high selectivity and moderate to high yields for a formal [3+4] cycloaddition. We envisioned
adopting siloxyvinyl diazoacetate (1b), which is more stable compared to vinyl diazoacetate 1a, to solve substrate limitations in this transformation (only electronic deficient imines 2 and aldehydes 3 offer the products 5 and 6 respectively) and develop an efficient method for the construction of newly functionalized seven-membered oxepins (8). Our progress in this area will be presented.

82. Polymorphism of the Secondary Explosive RDX Revisited
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The performance of the secondary explosive RDX depends on a variety of crystalline properties including material phase, density, morphology and internal defect structure. Though widely studied for many years, a detailed understanding of these solid-state properties with respect to the crystal growth environment remains incomplete. Of the four known polymorphic forms in the solid state, only the α and β forms are observable from solution growth under atmospheric pressure. Previous reports suggest that the infrequent appearance of β is due to its metastability and/or its limited number of growth solvents.

In this work, RDX was crystallized from a variety of different solvents and on 2D self-assembled monolayer (SAM) templates. Crystals grown were analyzed using a variety of x-ray diffraction and spectroscopy methods. Several new observations can be drawn from SAM-directed growth on this system: (a) β-RDX grows from a wide variety of solvents and can be stabilized for long time periods on SAMs, (b) preferred α-RDX orientations are observed on select SAM templates, and (c) the morphology and internal defect density of α-RDX vary significantly with the growth conditions. Understanding the intimate relationship between the growth conditions and the resultant properties of RDX is an important prerequisite to improving the performance of plastic bonded explosives.

83. Photochemical control of CTAB surfactant system through photoisomerization of cinnamic acid derivatives.
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Photoreheologial fluids (PR) are systems whose transitions from a free flowing sol state to a highly viscous gel state are controlled by light. The advantages of using light as a stimulus are the spatial and temporal precision, and wavelength specificity of photochemical reactions. Previously RagHAVan et. al.\textsuperscript{2} have reported a system wherein photolysis of trans-ortho methoxy coumarate (tOMCA) ions in cetyltrimethylammonium bromide (CTAB), caused a morphological change of the micelles from sphere to worm-like, inducing an increase in viscosity. The current study demonstrates that the relationship between the differential binding of cis and trans cinnamic acid derivatives to CTAB surfactants causes the rheological changes. This relationship is elucidated through 1D and 2D NMR studies, as well as through photolysis experiments. Furthermore, DFT computations identify specific structural changes in the isomers of the cinnamate derivatives that lead to differential binding.

84. Oxonium ylide formation and [1,2]-rearrangement to afford an oxybicyclo[4.2.1]nonane

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In our efforts to prepare oxobicyclononanes we have employed the hetero-Diels-Alder reaction between aldehydes and Danishefsky’s diene to give substituted tetrahydro-4-pyronones \textsuperscript{1}. Mukaiyama-Michael addition with vinyl diazoacetate \textsuperscript{2} provided functionalized diazo compound \textsuperscript{3}. Decomposition of this compound, catalyzed by rhodium(II) Lewis acids produces the oxonium-ylide and subsequent rearrangement to afford two diastereoisomers of oxobicyclo[4.2.1]nonane product \textsuperscript{4}. Control of diastereomer formation was made possible by increasing the size of the aryl group of the aromatic aldehyde for the overall synthesis, and results from this study will be presented.

85. Scale-up microwave-assisted synthesis for commercial applications

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Accel Synthesis is a unique contract company that provides chemical synthesis services using a combination of traditional methods and microwave technology to deliver milligram to kilogram quantities of custom chemicals to customers. Our proprietary microwave technology offers unparalleled speed, scalability and cost efficiency. This presentation details the recent work in our laboratory in which we have expanded the scope of scaled-up microwave-assisted chemistries. Examples include pharmaceutical intermediates and building blocks, monomers for OLED applications, and the total synthesis of alpha-Santalol, a natural product with pharmaceutical applications. Currently we have the capability to achieve production rates in excess of 50 kilograms per eight-hour period. The development of a production-scale microwave continuous-flow reactor will also be discussed.
86. Advances in siloxane-based coupling reactions: Investigation of novel 16-electron palladium(0) tri-olefin catalysts to promote allyl-aryl coupling

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Investigation into the role of ligand conformation and electronic properties in the coupling of an allylic carbonate and an aryl siloxane in the presence of novel 16-electron palladium(0) tri-olefin catalysts has been undertaken. By varying the ring strain present in the bidentate diene ligand, as well as by modifying the electron density present in the π-bond of the monodentate ligand, a variety of ligand-metal cone angles and binding affinities were examined in their ability to afford catalysts capable of providing the coupling product. This siloxane based palladium(0) coupling technology extends beyond basic unsubstituted allyl-aryl systems, having been shown to lend itself to the regio- and stereoselective coupling of advanced intermediates of pancratistatin and its derivatives.

87. Optimization of Dirhodium Caprolactamate Catalyzed Phenolic Oxidations with T-HYDRO

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Dirhodium caprolactamate is an extremely efficient oxidative catalyst for a wide range of substrates. Most recently it has been proven effective in the oxidation of phenols by tert-butyl hydroperoxide. Optimization of reaction conditions using butylated hydroxytoluene(BHT) showed a dramatic rate enhancement in aromatic solvents relative to oxidation in dichloroethane (DCE) media. The same, although less pronounced solvent effect, is observed for other catalysts capable of phenolic oxidation - RuCl$_2$(PPh$_3$)$_3$ and CuI. Conditions for this oxidative scheme were developed for a large scope of substrates.
88. Development of nanomolar affinity inhibitors of the *Yersinia pestis* Protein-tyrosine phosphatase (YopH)

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The protein-tyrosine phosphatase (PTP), YopH serves as an essential virulence factor for *Yersinia pestis* (*Y. pestis*), the causative pathogen of plague and a potential bioterrorism agent. In spite of the significant progress been made in inhibitor development against certain other phosphatases, YopH represents an important yet much less developed therapeutic target. Our current study reports the first $K_M$ optimization of a library of nitrophenylphosphate containing substrates for the purpose of generating a PTP inhibitor lead. A high affinity substrate identified by this method ($K_M = 80$ μM versus $K_M = 600$ μM for parent $p$-nitrophenylphosphate) was converted from a substrate into an inhibitor by replacement of its phosphate group with the non-hydrolyzable phosphoryl mimetic, difluoromethylphosphonic acid and by attachment of an aminooxy handle to provide a site for further structural optimization by oxime-ligation. A cocrystal structure of this aminooxy platform in complex with YopH allowed unambiguous assignment of its binding orientation and the identification of a conserved water molecule proximal to the ligand aminooxy group that was subsequently employed for the design of furanyl-based oxime derivatives. By this process a non-promiscuous high affinity ($IC_{50} = 190$ nM) inhibitor was developed that exhibited good YopH selectivity relative to a panel of phosphatases. The inhibitor showed significant inhibition of intracellular *Y. pestis* replication at a non-cytotoxic concentration. The current work presents general approaches to PTP inhibitor development that may afford significant utility beyond its immediate target.

89. Synthesis of natural product-like macrolides

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We are interested in the synthesis of natural product-like macrocycles that contain unique molecular architectures which can be exploited for their potential activity in biological systems. A new family of macrolactones, characterized by their fusion to a D-pyranose, is fused to the C1 and C5 positions of pyranose. The carbohydrate affords a one heteroatom bridge in the [n.3.1] bicyclic structure similar to that seen in amphidinolide O. The size of the major ring of the molecules varies between 12 to 14 atoms. The concise synthesis involves the acylation of 1-allyl glycoside and subsequent macrocyclization via ring closing metathesis. Structural analysis and biological screening of the novel natural product-like molecules are to follow.
90. **High-throughput screening of whole-cell *Mycobacterium tuberculosis*: Leads and hit follow-up**

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In an effort to identify both new drugs and new enzymatic targets in *Mycobacterium tuberculosis* (Mtb), we screened a 15,000 compound library against GFP-expressing Mtb. Initial hits were tested to determine minimum inhibitory concentrations (MIC). Spontaneously-resistant mutants were selected on compounds with MIC values <10 μM. After confirmation of a change in MIC value for the mutants, genomic DNA was extracted and the genome was sequenced to identify the single-nucleotide polymorphism (SNP) that confers resistance. Through this process we have identified both new potential therapeutic agents and as well as new enzymatic targets. Resistance mutations in transcriptional regulators and proteins involved in transport across the cell membrane have been identified, as well as novel targets involved in cell wall biosynthesis and nucleotide salvage.

91. **Chemoenzymatic modification of natural sophorolipids: development of novel antimicrobial agents**

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Sophorolipids consist of disaccharide sophoroses linked glycosidically to C18-chain-length fatty acids and are produced by fermentation of several fungi including *Candida bombicola*. In nature, they exist as open chain (at left) or lactonic (at right) forms with varying degrees of acetylation at the sophorose head group. Although they have natural antimicrobial activity, we have augmented this activity by chemical modification of the sophorose hydroxy and carboxyl groups to prepare a novel family of neutral and cationic surfactants. The consequences of these modifications as they attenuate the physical properties (including critical micelle concentration and self-assembly) and activity against a variety of agriculturally significant plant pathogens, will be discussed.
92. **Structure-based design of potent, selective and orally active p38α MAP kinase inhibitors**

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Anti-cytokine (e.g. anti-TNFα, anti-IL1) therapies based on biologic platforms have demonstrated significant clinical benefit against a variety of autoimmune diseases. This success energized the search for effective small molecule based inhibitors of cytokine production that could offer similar benefit with advantages that include reduced cost of goods and efficacy from oral administration. The MAP kinase p38α occupies a central role in inflammation, influencing the production of key inflammatory mediators as well as regulating many of their effects. Inhibition of p38α has emerged as an attractive target for anti-cytokine approaches. Our own efforts have led to the discovery of multiple scaffolds for the development of small molecule p38α inhibitors, including those based on the pyrrolo[2,1-f][1,2,4]triazine framework. Incorporation of aryl and heteroaryl ketones at the C6 position of the pyrrolotriazine, suggested by evaluation of X-ray co-crystal structures, led the discovery of potent and selective inhibitors of p38α. Further structure-based design efforts, starting from the pyrrolotriazines and related bicyclic templates, led to the discovery of a novel series of heteroaryl carboxamides as p38 inhibitors with improved properties. The structure-activity relationships, pharmacokinetics and efficacy in rodent models of acute and chronic inflammation will be presented.

93. **Local therapeutics for mustard-induced vesication**

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Pharmacological inactivation of fatty acid amide hydrolase (FAAH) or blocking the TRPV1 channels alleviates pain and edema associated with inflammation. Costa and Bettoni (2010) have reported a dual FAAH inhibitor-TRPV1 channel blocker, N-arachidonoylserotonin, displayed systemic (but not local) efficacy in the inflamed rodent paw model wherein irritation was induced by intraplantar injection of carrageenan. Our project requires local therapy at the site of inflammation induced by sulfur mustard and other chemo-vesicants and for this purpose we have discovered a new therapeutic class which combines FAAH inhibitors and TRPV1 blockers in a carbamate platform. These candidate therapeutics -- aliphatic-vanilloid carbamates -- suppress local edema and inflammation in a mouse ear model where the tissue insult was affected by phorbol ester (TPA) or chloroethyl ethyl sulfide (CEES). All compounds tested showed inhibition of FAAH but in a library of 62 analogs there was not a linear correlation of IC₅₀ to the percent suppression of inflammation measured in vivo. The replacement of aliphatic hydrocarbon chain by terpenes of known anti-inflammatory activity lead to some of the most potent analogs in the library. Synthetic approaches to members of the class and SARs in this family will be discussed.
94. Synthesis of new highly sensitive light emitting probes for biological and technical applications

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A variety of contemporary analytical platforms in technical and biological applications take advantage of labeling the objects of interest with fluorescent or luminescent tracers. Luminescent tracers take advantage of the unique property of some lanthanide metals to absorb and emit light. Long life time of lanthanide emission allows temporal gating of the signal, which avoids the short-lived background of interfering sample components. This property in combination with large Stokes shift contributes to extreme sensitivity of detection (ca. \(10^{-13} - 10^{-14}\) M), which makes lanthanide-based probes suitable for large variety of challenging tasks (e.g. intracellular detection of single DNA/RNA, or protein molecules, microbial pathogen detection in human specimens, tracing analysis, etc.). Luminescent probes include antenna fluorophore that absorbs the light and transfers the excitation energy to a lanthanide tethered to antenna through chelation. The probe also contains crosslinking group that allows covalent labeling of the molecule of interest. Despite great potentials of lanthanide-based tracers, the wide spread of the technology is impeded by very high price of commercially available probes, which is due to their complex structure. The goal of our research was development of new strategies for the synthesis of lanthanide probes. In the course of this work we synthesized new antenna-fluorophores, developed new methods for introduction of the crosslinking groups in the luminescent probes and elucidated the mechanisms of the chemical reactions leading to principal synthetic intermediates. We also synthesized new quinoline-based fluorophores with useful fluorescent properties and coupled their derivatives to DNA oligonucleotides using click chemistry to obtain sensitive hybridization probes. Synthesized compounds were characterized using NMR, steady-state and time-resolved fluorescence spectroscopy, as well as UV absorption spectroscopy.

95. Investigation of Complexes Formed Between Samarium Diiodide and Various Phosphoramides

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The complex formed between SmI\(_2\) and four equivalents of HMPA has evolved into one of the most versatile reagents for performing organic reductions, often with concomitant formation of carbon–carbon bonds. Although of great synthetic value, HMPA is known to be mutagenic in laboratory...
animals. This research group is engaged in the development of replacements for HMPA to be used in conjunction with SmI₂. The goal of this program is to find ligands that activate SmI₂ to a greater extent than HMPA but which are less mutagenic. Monodentate phosphoramides such as tripyrrolidinophosphoric acid triamide (1) and bidentate phosphoramides such as diHMPA (2) have been investigated in this context. Complexes of these ligands with SmI₂ have been investigated with respect to their structure and reactivity. The synthesis and utility of new mono- and bi-dentate phosphoramidate ligands will also be presented.

96. Advances in carbohydrate synthesis: Ionic liquid mediated formation of polyphenolic glycosides

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There has been recent interest in examining the therapeutic value of aromatic O-glycosides, which are frequently isolated as natural product extracts from traditional herbal remedies. Biologically active examples include flavonoid and coumarin anticancer agents that target VEGF, RSK, or Hsp90, and a number of antibiotics involve an aromatic aglycon conjugated to naturally occurring carbohydrates. Exploration of the structure activity relationships of these types of compounds predicates construction of aromatic-carbohydrate linkages. However, phenols are less nucleophilic than aliphatic alcohols under acidic conditions, are ambident nucleophiles that form C-aryl glycosides, and are often sterically hindered which prevents effective glycosidation. Herein, applications of ionic liquids to the challenges of aromatic glycosidation are described. Halide molten salts, such as 1-butyl-3-methylimidazolium chloride, were excellent media for O-glycoside bond formation under basic conditions and mild heating. The molten salts were easily recycled and used for multiple reaction cycles without loss of activity. N-heterocyclic carbene complexes were implicated as the promoters of the coupling, and the glycosidation reaction of phenols with tetra-O-acetyl-α-D-galactopyranosyl bromide promoted by in situ generated Ag-NHC complexes in ionic liquids was evaluated. Good to excellent yields were obtained using Ag-NHC complexes derived from imidazolium halide salts to promote the glycosidation reaction, whereas yields considered moderate to low were obtained without use of the silver carbene complex. Isolated N-heterocyclic carbene complexes derived from the ionic liquids 1-benzyl-3-methylimidazolium chloride and 1-(2-methoxyethyl)-3-methylimidazolium chloride were efficient promoters that selectively produced the β-O-glycosides in good yields with flavones, isoflavones, coumarins, and chromanone acceptors. Ionic liquids were also shown to be effective when employed in a dual role as phase transfer catalyst and solvent for biphasic, base-promoted O and S-glycosidation reactions. A new tailored ionic liquid, 1-hydroxyhexyl-3-methylimidazolium hexafluorophosphate was rationally designed to be immiscible with water and dichloromethane, which provided an advantage in ionic liquid recycling and product recovery via convenient triphasic extraction. The glycosidation reactions of a wide variety of substrates including phenols (17–79%), thiophenols (24–97%), chalcone (44%), and flavone (50–67%) were evaluated using this methodology.
97. Free radical scavenging and antioxidant activity of phenolic compounds from onion (Allium cepa)

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Six different types of onions available in the Kuwaiti market were analyzed for total antioxidant activity using different techniques such as Trolox equivalent antioxidant capacity (TEAC), malondialdehyde (MDA), and total phenolic content (TPC). These samples comprised of US onions white, US onions yellow, Indian onions red, Egyptian onions red, New Zealand onions golden and Saudi onions white. Layers from each onion bulb were manually cut and separated into three nearly equal portions, i.e., outer layers, middle layers and the inner layers. These samples were then macerated in a blender and freeze-dried for chemical analysis. The outmost layers of the bulb showed the highest concentration of antioxidant compounds and a distinct decreasing trend was observed towards the innermost layers in all types of onion samples. The onion samples studied showed variations in carbohydrate contents (glucose, fructose and sucrose), which would have important implications in affecting the flavor (sweetness and pungency) and the suitability of these onions for processing. The research findings presented in this report bring out an important observation about the distribution of antioxidant compounds with the highest contents in the outmost layers of the onions. Unfortunately, these layers are generally discarded by the consumers thus depriving them of the valuable nutrients, which must be prevented thru proper consumer education concerning the utilization of such important health-promoting phytochemicals. The free radical scavenging and antioxidative activity and their distribution in outer, middle and inner layers in some of the important varieties of yellow, white and red onions available in the local Kuwaiti market will be discussed in this research paper.

98. Probing of Tetracycline and Zinc Ion interaction

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Probing of Tetracycline and Zinc Ion interaction It has been confirmed that metal ions disrupt the bioavailability of tetracycline and its derivatives due to the formation of metal ion complexes. The location at which the metal ion chelation occurs has not yet been identified. One complex of interest is the tetracycline and Zinc ion coordination. We hypothesize that the Zn$^{2+}$ interacts with tetracycline at the regions depicted below (A,B,C,D) as in figure 1.

To probe the interaction of Zinc ions with tetracycline, we modeled and calculated the corresponding vibrational spectra. The calculations of the vibrational frequencies are carried out using the GAUSSIAN 09 software which applies the DFT methods with the RB3LYP/6-31+G (d) basis set. To visualize the results and analyze the calculated vibrational frequency spectra, we used the companion GAUSS-
VIEW tool. Adjacent to the theoretical aspect of the study, the sample are experimentally analyzed using Infrared and Raman spectroscopy. In order to identify the sites where Zn$^{2+}$ interacts to tetracycline we compared the results of our calculation to those obtained from the experimental data.

99. Probing Zn$^{2+}$-Tetracycline Using Vibrational Spectroscopy

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Tetracycline is a known antibiotic and an inhibitor of metalloproteinase enzyme. Little is known about which part of this large molecule is responsible for its antibiotic property as well as its inhibitor function. The latter might be attributed to the capacity of tetracycline to chelate metal ions. We began by looking at the role of the carboxyl group in tetracycline as possible sites of metal chelation. The project is designed to evaluate structure function relationship in tetracycline. To mimic the carboxyl group in tetracycline we used citrate. In order to fully characterize the interaction we looked at the effect of adding amino acid, like glycine, to the system. Earlier study has shown that the present of glycine decreases the interaction of the citrate with metal, Zn$^{2+}$ by forming a “zinc-amino acid and/or mixed-ligand complexes” (Sobel S., Haigney A., Conception T., and Kim M. (2008). The Complexation of Aqueous Metal Ions Relevant to Biological Application. 1. Poorly Soluble Zinc Salts and Enhanced solubility with Added Amino Acid. Chemical Speciation and Bioavailability, 20(2), 93-97). This particular work aims to characterize the Zn$^{2+}$-citrate interaction as a function of glycine concentration. To follow this interaction we used vibrational spectroscopy. Data obtained was compared to simulated vibrational spectra and discussed as it pertains to variation of interaction. Taken together the data helped to establish the molecular picture explaining the metal-ligand interactions in tetracycline.

100. Gold nanoparticles increase the liver toxicity of acetaminophen

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Broad research has been conducted on assessing the potential toxicity of nanoparticles when administered alone in various test systems. However, the possibility that nanoparticles may enhance the toxicity of other pharmaceutical agents has not been extensively explored. This study investigated the effects of acetaminophen metabolism and hepatotoxicity in Balb/C mice pretreated with a 5 mg/kg single dose of citrate-stabilized 10 nm gold nanoparticles. Seventy-two hours after gold nanoparticle administration, mice were given a single dose of varying concentrations of acetaminophen. Blood was collected at multiple time points, and the mice were sacrificed at either 5 or 24 hours following acetaminophen dosing. Multiple endpoints were evaluated, including histopathology, liver enzyme levels, glutathione concentrations, and acetaminophen metabolites. Preliminary results show an increased mortality associated with a single dose of acetaminophen following a single dose of gold nanoparticles. In addition, mice dosed with both gold nanoparticles and acetaminophen exhibited increased incidence and severity of microscopic liver damage 24 hours after dosing compared to mice that received either agent alone. In vitro results in rH4IIE rat hepatocytes show that gold has the ability to decrease glutathione levels. Therefore, the observed toxicity is thought to be due, in part, to acetaminophen depleting glutathione levels, causing a subsequent increase in the toxic metabolite N-acetyl-p-benzoquinone imine (NAPQI). These results suggest that nanoparticles may indirectly contribute to toxicity by interfering with the response to a secondary insult and also reveal the potential importance of additional studies in assessing the safety of nanoparticle-based drugs.
101. FT-IR spectroscopy characterization of *Bacillus subtilis* sporulation and bacteriophage infection in catabolite rich media

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*Bacillus subtilis* is an aerobic endospore forming bacterium found in a variety of terrestrial environments. *B. subtilis* sporulation is induced by adverse environmental conditions and exhibits a catabolite repressive phenotype. However, specific wild-type strains infected with spore-converting bacteriophages exhibit catabolite resistant sporulation. Thus infected cells induce sporulation pathways under conditions that would normally repress sporulation in wild-type uninfected cells. This phenomenon was examined using Fourier transform infrared (FT-IR) spectroscopy (4000-400cm⁻¹). Attenuated total reflection (ATR) FT-IR spectroscopy was used to detect biochemical and physiological changes induced in bacterial strains 313 and 168 with spore-converting bacteriophages, SP10 and PMB12. FT-IR spectroscopy demonstrated a nondestructive method to monitor cellular changes. Increase in the amount of aliphatic ester corresponding to changes in chemical functional regions of the cellular membrane were detected in spores formed from wild-type cultures compared with spores formed from infected cultures grown in catabolite rich media.

102. Context dependence of active-site residues in metabolic enzymes: Knowledge-based tools for enzyme redesign

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We applied computational tools that identify residues in an enzyme that may be interacting to confer substrate specificity. A pair of programs we are developing – Patterns and PyTRIP3D – examine the evolutionary changes that have occurred in a family of proteins with more than one substrate specificity and map those changes onto a protein structure. Changes that group together, in both sequence and three-dimensional space, are identified in the context of the enzymes’ substrate specificities. This provides a set of mutagenesis experiments to perform in order to swap the specificity of a member of the protein family. Here we discuss a set of mutations at the active sites of two metabolic enzymes in our model protein families: *E. coli* malate dehydrogenase (MDH) and *E. coli* aspartate aminotransferase (AATase). The experimental analysis compares the specificity of the enzyme variants for two possible substrates (oxaloacetate vs. pyruvate for MDH and Asp vs. Phe for AATase). For the first tests of the computational tools, analysis of each enzyme family was narrowly focused on an active site residue that has previously been implicated in substrate specificity, but whose precise role remains ambiguous. In malate dehydrogenase, we identified a small set of residues whose evolutionary patterns correlate with the active site Arg81. In aspartate aminotransferase, residues that covary with Val39 are being examined.

103. Intermediates in the biosynthesis of the antimicrobial phenazine D-alanylgriseoluteic acid

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D-alanylgriseoluteic acid (AGA) is a bioactive phenazine produced by certain strains of the biocontrol agent *Pantoea agglomerans*. This gram-negative bacteria and plant commensal is able to suppress outbreaks of the economically important fruit tree disease known as fireblight. The mechanism of
suppression is complex and involves both physical factors as well as chemical antagonists produced by *P. agglomerans* that are active against the fireblight pathogen, *Erwinia amylovora*. *P. agglomerans* is also an opportunistic human pathogen. Infections are most often associated with traumatic injuries involving vegetative matter such as impalings. Since phenazines are known virulence factors in other species, it is possible that AGA may have a role in both fireblight suppression and human infections. Preliminary data suggests AGA may also have potential as a novel scaffold for antibiotic development. A complete characterization of the ~13 enzyme AGA biosynthetic pathway will reveal what steps may be suitable for protein engineering experiments aimed at enhancing the potency of AGA. Here we present recent advances in delineating the biosynthetic pathway leading to AGA and describe the identification of two key intermediates using mass spectrometry.

**104. Small Molecule DNA Interaction using Fluorescence Spectroscopy under Different Salt Conditions**

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UV-Visible Spectroscopy and Fluorescence Spectroscopy were used to characterize the interaction between G-quadruplex DNA and porphyrins. The interaction of three G-quadruplex DNA sequences, d(T\(_4\)G\(_4\))\(_4\), d(T\(_4\)G\(_4\)T\(_4\))\(_4\), and d(T\(_2\)AG\(_3\))\(_4\), with porphyrins meso-tetrakis (4-((N-methylpyridyl)) H\(_2\)T\(_4\), and its Zinc derivative ZnT\(_4\), were studied under sodium and potassium salt conditions. UV-Visible Spectroscopy indicated that both H\(_2\)T\(_4\) and ZnT\(_4\) interact with G-DNA. Further Fluorescence spectroscopy data suggested that binding of G-DNA and porphyrins is dependent on salt type. Also, this study indicates that both H\(_2\)T\(_4\) and ZnT\(_4\) most probably bind to d(T\(_4\)G\(_4\))\(_4\) and d(T\(_4\)G\(_4\)T\(_4\))\(_4\) at the 3’ end of G-quartet, but that the binding to the end of d(T\(_4\)G\(_4\))\(_4\) is more effective due to the presence of G-quartet at the 3’ end. It is also suggested that the binding between porphyrin and G-DNA of sequence d(T\(_4\)G\(_4\)T\(_4\))\(_4\) is weaker due to a terminal 3’ thymine.

**105. Synthesis of an electron rich quinone methide precursor to expedite sequence-directed alkylation of DNA**

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A quinone methide (QM) is a very reactive electrophilic intermediate that can alkylate the most nucleophilic nitrogens in the bases of DNA reversibly. This reversibility has been used to construct sequence-directed alkylation reagents, but their reaction is slow. We have now synthesized an electron rich quinone methide precursor (QMP) to accelerate QM (re)generation for selective alkylation. The DNA-QMP conjugate was completely converted to DNA-QM self-adduct within 0.5 hour when the electron donating group was present compared to a period of 24 hours needed for a parent QM lacking the electron donating group. Alkylation study using the DNA-QM self-adduct with a single strand DNA target also showed that the electron rich self-adduct needed only half (2 days) as long as the unsubstituted self-adduct (4 days) to reach maximal alkylation of the target. This enhanced efficiency should shorten the time for a QM to take effect in a biological system.

**106. Photodimerization of thymine analogs to simulate the photodimerization implicated in skin cancer**

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In a bioorganic approach to understanding DNA photodamage implicated in skin cancer, thymine analog photodimerization was investigated. The effect of the thymine analog structure, hydrogen
bonding and π stacking effects on the efficiency of the photodimerization will be discussed. http://JulietHahn.com

107. Trapping reversible ortho-quinone methide - nucleoside adducts

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Electrophilic ortho-quinone methides (o-QM) can alkylate DNA and are generated during xenobiotic metabolism of a variety of compounds. From model studies based on nucleosides, o-QMs react most readily, but reversibly with strong nucleophiles. Their reaction is less efficient, but irreversible with weak nucleophiles. The hour time-scale of the reverse reactions complicates analysis of their products in DNA, which requires enzymatic digestion and chromatographic separation. Instead, a chemical trap utilizing bis[(trifluoroacetoxy)iodo]benzene has been developed to transform the reversible o-QM-DNA adducts into irreversible derivatives capable of surviving such analysis. Studies involving a model o-QM and 2′-deoxycytidine (dC) resulted in the isolation of an unexpected derivative after oxidative trapping. This derivative was rapidly formed by intramolecular cyclization, rather than the expected intermolecular addition of water. The final derivative should be sufficient for identifying the labile o-QM-dC adduct in DNA. Current studies are focused on the characterization of the oxidized 2′-deoxyadenosine (dA) and 2′-deoxyguanosine (dG) adducts.

Undergraduate Research Poster Session
Organizer: P. Deshong

108. Heterocyclic inhibitors of the helicase of hepatitis C virus

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The Hepatitis C virus (HCV) is a common chronic blood-born infection whose current standard treatment is not effective in a large percentage of patients; thus, there is a clear need for the development of better therapeutics. 1 and 2 exhibit similar low micromolar activity against HCV replication in replicons and with purified HCV helicase. It is hypothesized that 1 and 2 occupy the same binding site on the helicase, with the benzyloxy group in each occupying the same hydrophobic pocket. This then suggests that analogs of 1 and 2 that have a hydrophobic moiety in the 6-position of the naphthalene ring rather than the 5- or 7-position would be more effective binders, and thus better inhibitors. Accordingly, an efficient method for the production of 6-substituted analogs of 1 and 2 has been developed involving key 6-iodo intermediate 3. This compound allows for the introduction of diversity late in the synthesis, enabling the creation of a library of 6-substituted compounds through Pd-catalyzed coupling reactions. This will facilitate structure activity-relationship studies to help elucidate the spatial and electronic demands of the binding site on HCV helicase enzyme.
109. Effect of repair mutants on PAH-o-quinone induced mutations in p53

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Polycyclic aromatic hydrocarbons (PAH) are ubiquitous environmental pollutants that are found in charbroiled foods, car exhaust and are a major carcinogen in cigarette smoke. Benzo[a]pyrene (BaP), a representative PAH can be metabolized into three mutagenic products: radical cations, anti diol epoxides and PAH o-quinones. We have been studying, BP 7, 8-dione (BPQ) a PAH o-quinone, which damages DNA primarily via reactive oxygen species (ROS). Three distinct properties of p53 mutations observed in lung cancers are (1) the predominance of G>T transversions; (2) the presence of a strand bias and (3) mutational hot spots. The purpose of our study was to determine the mutation rate and pattern of p53 after treatment with BPQ in a yeast based reporter assay. In addition, we also wanted to determine if the DNA repair genes Ogg1 and Apn1 was involved in repair of oxidative damage caused by ROS generated due to exposure to BPQ. In order to determine the mutation rate, p53 cDNA was treated with BPQ and transformed into our yeast system which utilizes a red and white colony selection to determine the mutational rate. We did not find a significant difference between mutational frequency in wild type and apn1 yeast. However, mutation rates of ogg1 yeast were about 2-fold greater. The plasmids from the mutant p53 colonies were isolated and sequenced to determine the pattern and spectrum of mutations. In ogg1 cells, there were twice as many G>T transversions than wild-type cells. In apn1 yeast, the predominant change was again G>T, although at a reduced rate. Interestingly, we observed a strand bias, but only in the apn1 yeast, with the G>T transversions in the non-transcribed strand outnumbering the transversions in the transcribed strand by about 3:1. These data suggest that when base excision repair pathways are compromised, oxidative damage can cause a strand bias similar to that seen in smokers.

110. Effects of Retinoic Acid on CA-OV3 Ovarian Cancer Cells in Culture

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This research describes the effects of all trans retinoic acid (RA) when applied to a specific ovarian cancer cell line (CA – OC3). To determine the effect on cell growth, a cell count and a BCA protein assay were performed. The growth study consisted of plating out a large number of flasks (48) where half were treated once with RA and half were used as a control. Total cell number was obtained by counting the number of cells in the flask using a hemacytometer. The BCA assay used bicinchoninic acid, a color changing compound, to quantify the amount of protein in the flask. To study the effects of RA on the cell lipids, a phosphate assay was set up. The phosphate assay consisted of two parts: a separation using thin layer chromatography (TLC) and the quantification of phosphate (which utilized a color changing compound, the Fiske Subbarow reagent). The TLC plate separated the different phospholipids by polarity. Both the phosphate assay and the BCA assay used an UV-VIS Spectrophotometer to quantify the color in the solution. The cell count and the BCA assay both showed a reduction of cellular growth due to the application of retinoic acid. While the phosphate assay was not completed due to a poor percent recovery off of the TLC plate, a calibration curve was constructed to relate phosphate concentration with optical density (absorbance) using the UV-VIS Spectrophotometer.
111. Molecular Dynamics of Sarcin-Ricin Domain: Testing of the Variations of a New Force Field

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Ribonucleic acid (RNA) is a single stranded nucleic acid that folds upon itself to form secondary and tertiary structures. RNA folding studies lead to the understanding of many items including the disruption of function for proteins and DNA insertions or deletions. Previously, RNA experiments were conducted in the lab without advance knowledge of the dynamics of the system. Now, studies are first being conducted through the computational method molecular dynamics. These MD runs allows the scientist to view the kinetics of the system, predict the molecule stability, and much more. This allows for more successful lab experiments conducted on RNA.

The rat sarcin-ricin domain, an RNA motif, is being used in this experiment. The Sarcin-Ricin domain is found in the large ribosomal subunit in all three kingdoms of life. The domain is not classified by a sequence but by the tertiary shape, the stacking of the bases and the path of the backbone. Usually in a molecular dynamics run with this molecule a characteristic hydrogen bond between the 2' oxygen on the ribose of the extra helical base and the second oxygen on the phosphorus is lost. This is due to the force fields, used in previous simulation, not allowing for the bond to stay together. A new force field was used in the equilibration steps to test the stability of the hydrogen bond and whether the hydrogen bond stays after the simulations in the OL force field presented by Banas, et al. The domain was first run on Amber t-leap. This process added missing atoms to the RNA, neutralized the RNA with 29 molecules of KCl salt and K+ ions, and also surrounded the domain with molecules of water in the shape of a truncated octahedron. Equilibration runs relaxed the density of the RNA and allowed the water molecules to make closer interactions with the RNA. This presented us the opportunity to test the hydrogen bond within the presence of the moving water molecules.

112. Research work towards a new method of blending powder coatings colors

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Custom colors for powder coatings are produced through grinding methods that are expensive for small batch consumers. Current methods of blending powder coatings include the grinding of two different colored powder coatings to a superfine powder or by creating excessive amounts of the custom powder coating. Coating a metal surface with a physically mixed, solvent-less, powder coating combination of colors will result in a speckled pattern on metal surfaces. During experimentation, TGIC-polyester Bluestreak II™ and Sky White™ were dissolved and mixed in diethylphthalate (DEP). The resulting solution was a sky blue color, but contained a large amount of volatile organic compounds (VOCs). Dry powder coatings are environmentally friendly and do not contain VOC’s; thus blending powder coatings using an organic solvent was not a desirable option. Supercritical fluids have been previously used in the processing and production of powder coatings and polymers. The aim of this research was to create an alternative technique of blending two different colored powder coatings into one solid color by using supercritical ethane as the solvent.

Initial experiments began with painting metal surfaces with powder coatings. Painting a metal surface with powder coatings contains three particular steps: coverage, coating, and curing. An electrostatic spray charges powder coating particles, which then cling to a grounded metal surface (coverage). The metal surface is coated when heat is applied to melt the powder coating particles into a thick uniform film on the surface. During the curing step, the powder coating becomes a rigid, cross-linked thermosetting polymer.
The experiments performed included the testing of ethane in a critical point apparatus at different pressures and temperatures. When the pressure was raised in the critical point apparatus, the volume and temperature of ethane was measured. When conducting the experiment at 32°C and 48 atm, ethane became a supercritical fluid. Though this was not physically observable, the experimental data gathered was compared to NIST data for ethane’s phase diagram.

In the next set of experiments, powder coatings particles were added to the glass capillary of the critical point apparatus. During the first experiment with Bluestreak II™ powder coating, a glass wool plug was used as supporting material. The supercritical fluid interacted with both the Bluestreak II™ and the glass wool. A second experiment used alternating layers of Bluestreak II™, glass wool, Sky White™, and glass wool. During both of these experiments, there was no observable dissolved powder coating as well as no powder coating the glass wool. The final experiment included the four layers with the DEP added into the glass capillary in the presence of supercritical ethane. During this final experiment, the desired sky blue mixed powder coating was achieved. Though the sky blue powder coating was created, the mechanism of the color mixing was unresolved. Future experiments using polysiloxane or perfluoropolymer powder coatings will be conducted.

113. Mechanism of fluorescence quenching of wavelength shifter, BBQ induced by cobalt benzene-1,2-dithiolate
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The fluorescence quenching of large aromatic molecules by transition-metal ions is well documented, and in several cases, increased quenching has been observed by transition-metal ions in comparison with that of main group analogues as a result of their paramagnetic nature. With this in mind, we will investigate the quenching effects and mechanism of metal dithiolate complex ([(n-C₄H₉)₄N][Co(bdt)₂]) on the fluorescence of BBQ (7H-benzimidazo[2,1-a]benz[de]isoquinoline-7-one). Previously this group reported that an liquid scintillation cocktail with 1, 1, 4, 4-tetraphenyl butadiene (TPB) and metal dithiolate complex, caused an increase in fluorescence emission. In order to fully understand the TPB fluorescence quenching processes, in this work we will study the mechanism of quenching in the presence of metal dithiolate complex and a different wavelength shifter called BBQ. The reason why we choose this specific molecule, because not only it is also a wavelength shifter like TPB but in addition, it has a absolute maximum absorption at 382 nm, which leads to minimum absorption overlap with the metal dithiolate complex.

114. Use of Density functional theory to identify the metal complexes formed by zinc (II) and citrate in aqueous solution
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Coordination chemistry studies metal complexes, which consist of a central metal atom enclosed by neutral molecules or negatively charged ions. It sheds light on the medical applications of metals by studying their properties. Zinc, the second most abundant trace metal in the human body, is encountered in more than 300 enzymes covering all six enzymatic classes in different species of all phyla. In protein zinc-binding sites, the zinc ion coordinates with diverse arrangements of protein side chains, including the nitrogen of histidine, the oxygen of aspartate or glutamate and the sulfur of cysteine; among these, histidine is most commonly observed, followed by cysteine. Much is known about the coordination sphere of protein zinc-binding sites; however, the coordination chemistry of zinc in medically relevant non-peptide biomolecules, such as tetracycline, remains obscure. The purpose of this study is to gain insight on the coordination of Zn (II) with the three carboxylate groups of citrate and correlate it to the binding of Zn (II) to molecules with multiple carbonyl or carboxylate binding sites, like tetracycline. We modeled
the possible coordination complexes formed between Zn (II) and citrate at different molar ratios and obtained their spectral data by using Density functional theory calculations taking in account that Zinc (II) usually assumes a tetrahedral conformation due to its d^{10} configuration. We compared the theoretical spectra to our experimental data obtained through Fourier Transform Infrared spectroscopy and Non-resonance Raman spectroscopy. The theoretical data predicts that coordination of Zn (II) to citrate would cause a conformational change in this molecule to form a distorted tetrahedron around Zinc in the gas phase. Also, Zn (II) binding would shift the carboxylate stretching peaks to higher energy depending on the van der Waals distance between Zn (II) and the oxygens of the carboxylate groups according to the theoretical data. This shift of the carboxylate stretching peaks is also observed in the experimental data confirming Zn (II) binding to the oxygens of the carboxylate groups.

115. The Role of Retinoic Acid in the Regulation of HOX Genes in Ovarian Cancer Cell Lines

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All-trans retinoic acid (atRA) treatment has been shown to inhibit growth in the SCC-25 cell line (oral squamous cell carcinoma).\(^{1}\) Treatment with atRA resulted in a down-regulation in the expression of certain HOX genes.\(^{1}\) The research presented here describes the effects of atRA treatment on cell growth using two ovarian cancer cell lines: CA-OV3 and SK-OV3. Treatment with atRA inhibited the growth of the CA-OV3 cell line. This study was compared to results obtained when SK-OV3 cells were treated with atRA; SK-OV3 cells were resistant to atRA treatment and thus were used as a control. Subsequent RNA extraction, reverse transcription, PCR studies, and gel electrophoresis separations were performed to determine the effect of atRA treatment on the expression of specific HOX genes. Two HOX genes (HOX B9 and ALX1) did show changes in expression due to atRA treatment. Future studies would involve the analysis of different doses of atRA treatment, monitoring expression at different time points, and the treatment of additional ovarian cancer cell lines using atRA to determine if these cell lines are resistant or sensitive to treatment.


116. Development of Portable Water Filtering System for Communities in Underdeveloped Countries

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I investigated and experimented the effect of water purifying capability of home-made filtering system composed of pebble, sand, soil, and activated carbon. The home-made water filtering system showed effective water treatment capability by filtering suspended particles and reduce odor and clearing obvious impurities contained in the raw natural water samples taken form Chesapeake Bay Watershed.
117. Magnetic nanoparticles for drug delivery applications

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The use of magnetic nanoparticles as carriers for drugs has received much attention in the recent past. These drug-delivery vessels consist of a magnetic core coated with a thin organic layer that binds the drug in place. In this work magnetic nanoparticles based on manganese oxide were synthesized using reverse micelle method and characterized using powder X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). Doxorubicin, a cancer drug was attached to these nanoparticles by first modifying with an amino group containing silica coating. The attachment of this drug was observed with Fourier Transform Infrared (FTIR) spectroscopy, and Raman spectroscopy.

118. Electrochemical glucose sensor: Redox polymer in β-cyclodextrin inclusion

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A sensitive electrochemical method for detection of glucose is being developed. In this method, osmium based redox polymer was included in a β-cyclodextrin. The inclusion complex was followed using Fourier Transform Infrared (FTIR) spectroscopy. The inclusion complex containing the redox polymer was attached onto glassy carbon electrode, and Gox was casted onto the electrode. The redox polymer was found to communicate with glucose oxidase as observed for the catalytic current in presence of glucose. This sensor arrangement was found to be stable over several weeks with excellent reproducibility.

119. Cytochrome c Catalyzes a Reaction Between Ferrous Sulfate and Hydrogen Peroxide

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Multilayer films of cytochrome c and poly(4-styrene sulfonate) were constructed using the layer by layer method of self adsorption on a gold electrode. Cytochrome c was initially linked to a gold surface using a mercaptoalkanol/alkanoic acid promoter layer that was covalently linked to the electrode via a Au-S bond. Upon the addition of FeSO4 and H2O2 large catalytic peaks corresponding to oxidation and reduction were observed with cyclic voltammetry, and which decreased upon subsequent scanning and addition of H2O2. After some time, an insoluble product was observed in the electrochemical cell.

120. Rheology versus structure in hydrotalcites

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Layered double hydroxides, also known as hydrotalcite-like compounds (HTs), are a class of layered materials. Structurally, they consist of positively charged metal hydroxide layers (brucite-like layers) separated by charge-balancing anions and interlayer water. The formula of HTs can be expressed in general as \([M^{2+}_{x+y}M^{3+}_{x-y}(OH)_2][A^{n-}\times\times\times m\text{H}_2\text{O}],\) where \(M^{2+}\) and \(M^{3+}\) are divalent and trivalent metal ions, \(A^{n-}\) is an interlayer anion and \(x\) is the \(\frac{[M^{2+}]}{[M^{2+}]+[M^{3+}]}\) molar fraction. HTs have prospective in a wide variety of applications, including use as anion exchangers and catalysts, in medical applications as antacids and for controlled release, and in polymers as stabilizers and nanocomposites. HTs have
been synthesised by coprecipitation, by mixing an alkaline solution and a mixed solution containing
divalent and trivalent metal cations. This method forms large aggregates of sheet-like HT crystal-
lites that are necessary to understand fundamental HT structure and properties. Rheology was suc-
cessfully applied since HTs are a system where the rheological response depends strongly on the
microstructure. Primary HT particles usually exhibit plate-like morphology, very suitable materials for
rheological investigations. Rotational rheometry measurements in terms of elastic ($G'$) and viscous
($G''$) moduli as a function of applied stress have been performed. Rotational rheometry was proven
to be a very sensitive method that detected very accurately the slightest change in particle arrange-
ment and their structure, as it evolved with temperature.

**Synthetic Chemistry**

**Organizer:** C. Wolf

**121. Adventures in oxidative coupling**

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Inspired by Nature’s use of oxidative couplings to construct carbon-carbon and carbon-nitrogen
bonds in many natural products, we have undertaken studies of such reactions. The development
of a highly enantioselective oxidative binaphthol coupling reaction and a highly enantioselective N-
arylation reaction, both of which use oxygen as the terminal oxidant will be discussed. Preliminary
work on the development of regioselective and asymmetric phenol couplings will also be described.
Applications to the synthesis of chiral natural products including nigerone, hypocrellin, and cercospo-
rin will be presented.

**122. Cucurbit[n]uril molecular containers**

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This talk will describe the mechanism of the formation of cucurbit[n]uril (CB[n]) molecular contain-
ers. We use this mechanistic knowledge to prepare new CB[n]-type containers that have a variety
of exciting structures (e.g. double cavity, chiral, acyclic) and describe their recognition properties.
The talk will also describe initial steps toward the use of cucurbit[n]uril molecular containers in drug
delivery applications.

**123. Concise enantiospecific, stereoselective syntheses of (+)-crispine A and its
(−)-antipode**

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United States ; Balazs Gyimothy²; Sang Q Lam¹; Ruifang Wang¹; Feryan Ahmed¹; R Jason Herr¹. (1) Medicinal Chemistry, Albany Molecular Research Inc., Albany NY 12084, United States (2) Chem-
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An enantiospecific and stereoselective total synthesis of the natural product (+)-crispine A has been
demonstrated employing a Pictet-Spengler bis-cyclization reaction between a commercially available
enantiopure 3,4-dimethoxyphenylalanine derivative and 4-chloro-1,1-dimethoxybutane to preferen-
tially provide the cis tricyclic adduct. Decarboxylation by a convenient two-step protocol provided the
enantiopure natural product in three steps with an overall isolated yield of 32% from the amino acid.
The unnatural antipode (−)-crispine A was similarly prepared in three steps from the commercially
available (S)-(−)-amino acid.
124. Optically active 1,1′-spirobiindane-7,7′-dion (SPINOL)-based phosphoric acids as highly enantioselective catalysts for asymmetric organocatalysis

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The synthesis of a series of optically active 1,1′-spirobiindane-7,7′-dion (SPINOL)-based phosphoric acids and their application as enantioselective catalysts for the reactions of indoles with aldimines and beta,gama-unsaturated-alpha-ketoesters are presented. Our study provides a family of promising chiral phosphoric acids to the asymmetric organocatalysis toolbox.

125. Peptoid oligomers: Stereodynamic folds and stereoselective functions

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Peptoids are a family of peptidomimetic oligomers composed of N-substituted glycine monomer units. Peptoids are an example of “foldamer” molecules, as even short oligomers can mimic polypeptide secondary structures such as helices and hairpin turns. We seek to develop a folding code for peptoids that would allow us to reliably associate particular peptoid monomer sequences with a specific three dimensional structure. Despite the structural similarities between peptoids and peptides, the rules for folding are likely to be distinctly different. The peptoid backbone lacks chiral centers and the capacity to form a hydrogen bond network. We describe recent efforts to synthesize functional peptoids, including oligomers exhibiting enantioselective catalysis and biological activity of potential therapeutic importance. In addition, we demonstrate that peptoids incorporating ortho-substituted N-aryl side chains exhibit axial chirality and form stable atropisomeric species. These results establish that chirality can be a dynamic characteristic of folded peptidomimetic systems.

126. Origin of C–H Oxidation Byproducts in Reactions of Glycal Metalla Acyl Nitrenes

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Metal-complexed acyl nitrenes derived from glycal 3-carbamates are useful for the synthesis of 2-amino sugars by intramolecular addition of the nitrene to the glycal alkene. With certain glycal
substrates, particularly glucal and galactal derivatives, we have also observed formation of dihydro-
pyranone byproducts, corresponding to oxidation at the C-3 position. Because our usual conditions
for metallanitrene formation include an iodine(III) oxidant, it was unclear whether dihydropropyranone
formation was proceeding via the nitrene intermediate or was due to a separate iodine(III)-mediated
process. We have now generated rhodium- and copper-complexed metallanitrenes from a glucal N-
toslyoxycarbamate, in the absence of any iodine(III) oxidant, and we have found that dihydropropyra-
none formation still occurs. These results are consistent with a nitrenoid-mediated pathway for C–H
oxidation, possibly through hydride transfer to the metallanitrene.

![Chemical structure]

127. Microwave-assisted one-pot three component synthesis of isoquinolines by
a coupling-annulation sequence
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A palladium-catalyzed microwave-assisted, one-pot, three-component reaction for the synthesis of
isoquinolines has been developed. The reaction is carried out in two steps by a coupling-annulation
sequence from ortho-bromoarylaldehydes/ketones, terminal alkynes and ammonium acetate. Am-
monium acetate is used as the ammonia source for the annulation reaction. A variety of substituted
isoquinolines have been prepared in good to excellent yields.

![Reaction scheme]
128. Aryl ketone synthesis via tandem orthoplatinated triarylphosphite-catalyzed addition reactions of arylboronic acids with aldehydes followed by oxidation

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Tandem orthoplatinated triarylphosphite-catalyzed addition reactions of arylboronic acids with aldehydes followed by oxidation to yield aryl ketones is presented. 3-Pentanone was identified as a suitable oxidant for the tandem aryl ketone formation reaction. By using microwave energy, aryl ketones were obtained in high yields with the catalyst loading as low as 0.01%.

New Approaches to Teaching Chemistry II
Organizer: S. Sinex

129. Discover the ChemEd DL: Digital resources for the high school chemistry teacher and student

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Interested in using digital resources in your classroom? Discover the multitude of free digital resources found at the Chemical Education Digital Library (ChemEd DL), a Pathway project of the National Science Digital Library (NSDL). The ChemEd DL collection provides exemplary digital resources, tools, and online services to aid in teaching and learning high school chemistry. Throughout the presentation we will explore the ChemEd DL’s innovative collection including Models 360, ChemTeacher, the award-winning Periodic Table Live! and so much more. In one session participants will find new digital chemistry resources and learn how to integrate them into their classroom curriculum. Ultimately, the ChemEd DL will be the place on the Web to find or share digital content for chemical sciences education. Participants will learn how they can use, contribute, and share chemical education materials through ChemEd DL.

130. “Common Core” standards, student test scores in math computation in the mid-Atlantic states, and the implications for chemistry instruction

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Solving calculations is a focus of initial chemistry courses. Nearly all mid-Atlantic states have adopted the new “common core” K-12 math standards. Will these standards impact student preparation for the math of chemistry?

This paper will compare the new common core standards to the prior standards for teaching math computation in mid-Atlantic states. Test score data in math computation for students in mid-Atlantic state will be presented which shows that state scores in math have most often decreased dramatically, though in some districts scores have increased. Differences in standards and curriculum that may have contributed to those trends will be noted.

Opportunities for those concerned with science education to voice their views on state K-12 standards and testing that impact student learning in the physical sciences will also be reviewed.
131. Assessing student learning in online general chemistry class

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The online version of General Chemistry taught at Anne Arundel Community College has a set of learning outcomes developed by the Chemistry Department. These are listed in the course syllabus for students to use as guidelines. The learning and assessment activities used in the course are listed in the individual modules. Each module is linked to a set of learning outcomes and learning objectives which in turn link to the content of the course.

How well students achieve learning outcomes depends on a number of factors including:

- The extent of mentoring and guidance by the instructor
- Assessment methods used to determine the extent of achievement of learning outcomes
- Tools used to deliver the content and to assess student learning
- Time invested by students to learn the content and their ability to demonstrate their grasp of the content
- Student’s ability to assess their own learning using the methods and tools provided in the course

The presenter will share a number of instructional strategies including student self-assessments, some traditional and accepted and some experimental, to engage students in an online science course. The session will include feedback received from students on the effectiveness of instructor’s strategies. The audience will have an opportunity to participate in informal discussion to share their strategies to promote student engagement in online science classes. The session includes a short PowerPoint presentation to guide the audience. A set of useful handouts will be shared with the audience.


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The ability to write about laboratory work is a crucial skill for chemists in industry, government, and academia. More broadly, effective communication is essential for success in almost every profession. Despite its importance, writing instruction is often absent or minimal in first year college chemistry courses. Collaboration between a writing fellow from the City University of New York Graduate Center and two chemistry professors from the New York City College of Technology led to the development of a method of explicit laboratory report writing instruction. The method is called directed-self inquiry because it teaches writing by emphasizing habits of self reflection. Directed self-inquiry associates key questions with each of the standard sections of a laboratory report (title, abstract, introduction, experimental, results, discussion, conclusions, references). Initially, the questions are presented in a worksheet format. For example, students learn to write the abstract by answering the following questions:

1. What did you do and why?
2. What were the most important results?
3. What can you conclude based on these results?

Students answer these questions on their own at home and use their answers as a scaffold for constructing the report they hand in. Eventually, students develop the habit of asking themselves these questions as they prepare to write. The lab report structure and associated questions are introduced
section by section. Students hand in weekly writing assignments. Feedback on each assignment is
provided during a weekly one-on-one conference with the professor. This conference lasts approxi-
mately three minutes and takes place during the laboratory class. Directed self-inquiry was imple-
mented on the pilot scale in fall 2010 in two sections of introductory college chemistry laboratory at
the New York City College of Technology (28 students total). Student attainment of report writing
proficiency was assessed using a rubric focused on competency in the structure, style, and content
of each laboratory report section. After one semester of instruction, 68 % of the students achieved
a score of 65 % or better on their final laboratory report. While additional studies are necessary to
compare the efficacy of directed self-inquiry to other methodologies and to assess the role of the
professor, the initial results are promising.

133. Mass, measurement, materials, and mathematical modeling: The nuts and
bolts of extrapolation

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A simple initial experiment for any chemistry or physical sciences class is presented. Students, work-
ing in groups, determine the mass of a bolt indirectly by extrapolation from massing the bolt with
one to five nuts on it and determining the equation of the line. Students gain experience with the
balance, graphing data, and then analyzing results using algebraic skills. They calculate percent error
after measuring the bolt’s mass directly. Groups enter data into a web-based form and the data can
be examined by the class using Google Docs in a collaborative manner. Then they use an interactive
Excel spreadsheet to compare their results to the best-fit line obtained by linear regression (pre-built
into the spreadsheet for novices). In the spreadsheet, they further explore the model to gain an un-
derstanding and examine the influence of scatter (error) in the data and material density. The activity
introduces students to mathematical modeling, an important scientific process, and online collabora-
tion. This work is supported by the Howard/Hopkins/PGCC Partnership for Research and Education in
Materials (PREM), funded by NSF Grant No. DMR-0611595.

134. Introducing Nanotechnology to Undergraduate Chemistry Curriculum

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Nanotechnology owing to its promising applications has received tremendous attention in the past
decades. As building blocks in nanotechnology, various methods have been developed to fabricate
nanostructures of well-defined compositions. Physical and chemical properties are size-dependent
over a certain size range specific to the material and property. When a particle of gold metal is similar
in size to wavelengths of visible light (400–750 nm), it interacts with light in interesting ways. The
color of a gold nanoparticle solution depends on the size and shape of the nanoparticles. This Activ-
ity introduces students to the unique properties of nanoscale materials through exploration of size-
dependent optical properties of gold nanoparticles. Students determine that a gold nanoparticle solu-
tion functions as an electrolyte sensor because electrolyte-induced aggregation of the nanoparticles
results in a dramatic color change. In this regard a solution of 1.0 mM HAuCl₄ was used at boiling
temperature and then a 38.8 mM solution of sodium citrate was added to the gold solution along with
stirring until it is a deep red color. The sodium citrate reduces the Au ions to nanoparticles of Au metal
which forms nanoparticle. NaCl, KI, household liquid and sugar was added to gold nanoparticles to
explorer it as a chemical selective sensor.
135. Arose Student’s Curiosity Using Science Lecture Demonstrations

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In an introductory level science class, it is always important for the instructor to get students’ attention and interest when a scientific topic is discussed. As a method to help non science major student to arise their curiosity in a science class, science lecture demonstrations were adopted in the lecture. For each section of the class, a designated demonstration was prepared to manifest the text in a tangible manner as well as to bring more life and excitement into the classroom. When the student’s curiosity is peaked, their attention will be focused. Furthermore, it will promote their thinking and understanding of the scientific concept. A student survey about demonstrations revealed these positive influences. The selected demonstrations were also tested and evaluated using eight detailed criteria. These criteria include ease of preparation, conceptual relevance, and reproducibility, which are all factors into the students understanding and development of comprehension. The evaluation of the demonstrations can be used as a guideline for further investigation.

136. Collaborative learning in a private high school second year chemistry class

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Inquiry-based learning gives students the chance to apply concepts learned in class to complex problems beyond the classroom. We augmented the curriculum of our Advanced Chemistry 2 Honors class by partnering with academic, governmental, and industrial institutions to give students an appreciation for the intellectual challenges and rewards characteristic of scientific research. The year began with a survey of student interests, consideration of likely projects and partners, and subsequent student election of individual and group projects in such areas as biodiesel synthesis from school-generated waste cooking oil, “greener” synthetic chemistry, and analysis of fruit samples for pesticides. We then sought out and engaged specific collaborators outside of the school to provide expertise and analytical capabilities to support these projects. Students continued work on their projects throughout the school year and gained valuable insight into post-secondary work and study.

137. It’s in the bag: New approaches to teaching science

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An animation of osmosis using a “bag” made from dialysis tubing placed in “solutions” of different concentrations. The dialysis tubing bag provides a semi-permeable barrier to two sizes of molecules. The molecules are represented by large red circles and smaller green circles. Using Adobe Flash CS4 Professional, I developed a series of images showing a membrane allowing small green circles to pass through, but not the larger red circles. By illustrating relative concentrations of the circle molecules, I animated the effects of isotonic, hypertonic, and hypotonic solutions on each bag. In addition, I placed the flash animations into an interactive Microsoft Power Point presentation in order to teach students how solution concentrations affect diffusion, how a semi-permeable membrane affects osmosis, and how tonicity affects a cell.
138. ChemEd DL: High quality online chemical education resources

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ChemEd DL, the Chemical Education Digital Library, is the place to go on the Web for chemical education resources. ChemEd DL includes: an interactive, pedagogically designed periodic table; a collection of molecular structures that can display symmetry, vibrations, and molecular orbitals; a wiki in which you can collaborate on a textbook that emphasizes the applications of chemistry topics to other disciplines and everyday life; a way for busy high school teachers to find online resources for teaching each topic of the high school curriculum; and a course management system that can be used by anyone to design and present online courses. This presentation will highlight the interactive periodic table, the collection of molecular structures, and the general features of the ChemEd DL portal.

Graphene Chemistry
Organizer: Y. Wang

139. Growth Mechanism of Well Aligned Single-walled Carbon Nanotubes on Quartz Substrate

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Even though the devices made from individual nanotubes have shown outstanding performances such as high mobility, high current, high thermal conductivity, good chemical and mechanical stability, the high hope for the next generation of carbon nanotube based electronics is hampered by several major problems. Among them are the lack of reliable methods to control the alignment and position of nanotubes as well as and perhaps most problematically, the simultaneous growth of nanotubes with different chiralities, yielding random mixtures of metallic and semiconducting nanotubes. Even though the post-growth separation of metallic from semiconducting SWNTs have made good progress, the alignment and assembly of the separated nanotubes into devices are still challenging and not suitable for large scale fabrication. Consequently, a method that can directly produce well aligned arrays of pure semiconducting nanotubes is thought to be the ideal choice for large scale fabrication of nanotubes FETs. In this talk, we show that such a method is not a dream. We developed a chemical vapor deposition (CVD) approach, which allows selective growth of high-density arrays of well-aligned SWNTs with almost exclusively semiconducting SWNTs. Analysis of the samples shows that at least over 95% of nanotubes are semiconducting. This method demonstrates great promise to solve two of the most difficult problems which limit application of carbon nanotubes in nanoelectronics – the coexistence of metallic and semiconducting nanotubes in samples produced by most, if not all, growth methods and the simultaneous control of the alignment of the nanotubes.

140. Electrical conductivity of surfactant modified carbon nanotubes

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Carbon nanotubes modified by various surfactants have been made into thin films. The thin film electrical conductivity was measured to understand the effect of surfactant structure and content on electrical conductivity. Spectroscopic characterization of the surfactant content in the carbon nanotube thin films will be discussed. http://JulietHahn.com
141. Ultrahigh concentrations of individually-dispersed single-walled carbon nanotube solutions enabled by a co-dispersant

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Single-walled carbon nanotubes were individually dispersed in aqueous solutions of sodium dodecylbenzene sulfonate (SDBS) using the surfactant dispersion technique. Sucrose was added as a co-dispersant which significantly increased the efficiency of the dispersion method. Over three times more raw nanotube material was converted to individually-dispersed nanotubes in the presence of sucrose. This increased percent mass conversion remained constant even as the initial loading mass of raw nanotube material was increased to unprecedented amounts. Spectroscopic results verified that as the loading mass was increased, the concentration increased linearly and the nanotubes in solution stayed individually dispersed. Constant conversion efficiently allowed for nanotube solution concentrations in the g/L range simply by increasing the initial loading mass. Individually dispersed nanotubes with concentrations in this range were previously attainable only in superacids. Unlike superacids, our SDBS and sucrose combination is more environmentally benign and may open opportunities for envisioned applications demanding high concentrations and biological-inert processing.

142. Chemical modification of carbon nanofillers in high performance polymer composites

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Composites are widely used in many military and commercial applications including lightweight helmets, body armor, sporting goods, and vehicular armor systems. Other applications may include electrically conductive or dissipative materials and supercapacitors. Important factors in mechanical performance are even distribution of filler and elimination of voids in the composites. Both of these defects can lead to premature failure under loading. In this work commercial nanofillers including Carbon Nanofiber (CNFox), oxidized and exfoliated Graphene (Grox) and Nanodiamond (ND) were chemically modified to improve their wetting properties to polymers and reduce voids and defects in composite systems. The new techniques allows rapid reactions under relatively low temperature conditions on filler surfaces and in bulk polymers without the generation of volatile reaction products such as water or methanol. This reaction scheme can also be applied to a range of fillers (including carbon nanofiber, CNF) to enhance dispersion and reduce cluster and void formation in processed composites. Composite samples were made with simple melt extrusion with isotactic polypropylene and polyester. Solution spun experiments were done with polysulfone. Samples were characterized by XRay Tomography, XRD, SEM and DMA tensile tests. At the freeze-fractured interface, treated CNF is clearly visible, dispersed and weakly aligned parallel to the melt flow. Above about 2 weight % levels for all fillers, more voids appear in elongated fashion, mostly between clusters of filler. The commercial carbon nanofiber was treated with functional organosilanes. This treatment anchors the silacyclobutane groups to the oxygen reactive sites and reduces the polarity to more closely match that of the non-polar polymers. The X-Ray tomographs were done for CNF loadings of 0.5 to 3 wt %. No detectable voids are present until loadings of 2 % and higher. At higher loadings the fibers are not easily drawn from the melt phase. The SEMs shows the differences in melt-spun polypropylene and solution-spun polysulfone composites. The near defect-free sample on the left has uniformly distributed CNF. The polysulfone-CNF composite, however shows many voids on several size scales. These filler modifications shown here are intended to help dispersion by reducing the polarity of the fillers. The next steps will be incorporate the silane units shown in Figure 1 and subsequently thermally
treat the composite to activate crosslinking at the filler surface. Similar treatments were shown previously to improve dispersion, but these new treatments allow thermal crosslinking in polymers with higher processing temperatures. Alternative processing techniques with other polymer are also being explored.

143. Using chemically modified graphene for electronics and sensing

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Unmodified graphene has many superlative mechanical and electronic properties that have been heavily researched. While exploration of these intrinsic properties continues to amaze, realizing graphene’s full potential still requires understanding and controlling its chemistry. For biosensors, attachment sites for biomolecules must be made. For electronics, band gaps must be opened by appropriate chemical functionalization. For mechanical oscillators, membranes must be attached to the supported substrate, and so on. I will discuss work by NRL to develop a wide range of chemically-modified graphenes (CMGs), briefly discuss their potential applications, and then focus on two particular applications. First, I will discuss using heatable AFM probes to localize chemical reactions. This technique writes graphene nanoribbons by locally reducing a CMG back to graphene. For example, reduced graphene oxide shows an increase in conductivity up to four orders of magnitude as compared to unmodified material. Variably conductive nanoribbons with dimensions down to ~12 nm have been produced in oxidized graphene films in a single step that is clean, rapid and reliable. Secondly, I will discuss generating CMGs with primary amine functional groups. Films of this material are the basis for sensitive, robust, and inexpensive biosensing.

144. Electronic and magnetic properties of a line defect in graphene

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Although graphene exhibits excellent electron and thermal transport properties, it does not have an intrinsic band gap, required to use graphene as a replacement material for silicon and other semiconductors in conventional electronics. The band structure of graphene with its two cones near the Fermi level, however, offers opportunities to develop non-traditional applications. One such avenue is to exploit the valley degeneracy in graphene. In this presentation, I will present a two-dimensional valley filter based on scattering of electrons and holes off a recently observed extended line defect [1]. The transmission probability depends strongly on the valley pseudospin and the angle of incidence of the incident quasiparticles. Quasiparticles arriving at the line defect at a high angle of incidence lead to a valley polarization of the transmitted beam that is near 100%.

I will also discuss recent results obtained from both first-principles and semi-empirical methods showing that the extended line defect gives rise to ferromagnetically coupled local moments. The ferromagnetism can be understood from a symmetry analysis of the boundary-localized eigenstates. The symmetry requires that the principal moments couple ferromagnetically both along and across the line defect, leading to approximately 2/3 more spin-up electrons and than spin-down electrons per repeat unit along the line defect.

This work was supported by the Office of Naval Research, directly and through the Naval Research Laboratory.

145. Functionalization of single-walled carbon nanotubes for applications in energy and medicine

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Single-walled carbon nanotubes (SWCNTs) have shown great potential for use in applications ranging from photovoltaic devices to drug delivery. Here we report covalent chemical functionalization of SWCNTs that results in nanotubes with highly advantageous properties. First, functionalization of oxidized SWCNTs with aromatic compounds such as benzene and phenol through a Fischer esterification has been achieved. Mixtures of these functionalized SWCNTs and the conducting polymer P3HT show bulk conductivities that are an order of magnitude greater than those of mixtures of unfunctionalized SWCNTs and P3HT. These functionalized SWCNTs are expected to improve charge transfer in SWCNT/P3HT bulk heterojunction photovoltaic devices. Second, functionalization of SWCNTs with the antiviral drug acyclovir through a multistep synthetic process involving the amino acid cysteine has been achieved. The acyclovir-functionalized SWCNTs exhibit significant antiviral activity against herpes-simplex-virus (HSV) infected cells. The results of these two projects demonstrate the importance of exploring the chemistry of SWCNTs.

146. Outerwall-selective Functionalization of Double-Walled Carbon Nanotubes for Electronic Devices Applications

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Double-walled carbon nanotubes (DWNTs) were selectively functionalized to the exclusion of inner tubes using diazonium chemistry. Even after the outer walls were covalently functionalized to the point where their Raman radial breathing modes completely diminished, the inner tubes exhibited intact Raman modes and the characteristic optical absorption peaks due to electronic transitions between van Hove singularities in density of states. After functionalization, DWNT thin films retained approximately 66% of their electrical conductivity, more than 100 times better than similarly functionalized single-walled carbon nanotubes. These results suggest the possibility of high performance DWNT electronic devices with important benefits of tailored surface chemistry and protection from outerwalls.

147. Simultaneous conductivity and solubility of double-walled carbon nanotubes

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Double-walled carbon nanotubes (DWNTs) were selectively oxidized on the outerwall to afford water solubility, while simultaneously retaining the graphitic integrity and electrical conductivity of the inner-tube. This scalable wet chemistry, by homogenous dispersion in oleum and limited nitric acid oxidation, circumvents the unattractive tradeoff between solubility and conductivity of covalently functionalized single-walled carbon nanotubes (SWNTs). Outerwall selectively oxidized DWNTs (oso-DWNTs) were characterized with UV-visible-NIR spectroscopy, Raman scattering, X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). These results show a positive cor-
relation between functional degree and water solubility with the relative reactant concentration and reaction times. Electrical conductivity of oso-DWNT thin films was retained 65% better than identically oxidized SWNTs, a phenomena attributed to electrical percolation pathways between the inner and outerwalls.

Fig. 1. Electrical percolation of oso-DWNTs via the inner-tubes. (A) The conductive pathway is disrupted in covalently functionalized SWNTs, but intact DWNT inner-tubes and regions of the outerwall extend the electrically conductive pathways. (B-C) TEM image showing thin film networks and two oso-DWNTs in contact.

148. Perfect marriage between NMR and SAXS for structure determination in solution

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NMR spectroscopy is a versatile method to study both structure and dynamics of biomacromolecules in solution. NMR measurements are based on perturbation of local magnetic fields of nuclei in a magnetic field. Consequently, they are mostly short ranged and contain little direct global dimensional information. NMR spectroscopists traditionally reply on large number of semi-quantitative distance restraints, combined with residual dipolar couplings, to determine three-dimensional structures of biomacromolecules. This approach works well provided that chemical shift assignments are known and a large number of distance restraints can be derived as in the case of structure determination of proteins and small RNAs, but has limited success in large RNAs or multi-component complexes. In contrast, small angle X-ray scattering (SAXS) data contains information of global dimension and shape of biomacromolecules but lacks information about local structural details. Therefore, NMR and SAXS complement to each other. For the past several years, our laboratory has developed several new methods of combined use of NMR and SAXS for structure determination of complexes and large RNAs. Those include the methods 1) to determine Global Architecture from SAXS and RDCs (GASR), 2) to determine Global structure from Global restraints (G2G), and 3) to interpret Nuclear Overhauser Effect spectroscopy (NOESY) without prior knowledge of chemical shift assignments for high-resolution structure determination of large RNAs. The combined use of NMR and SAXS overcomes intrinsic limitation of NMR spectroscopy and represents a perfect marriage in solution.
149. Small-angle x-ray scattering and NMR-based structural analysis of riboswitches in solution

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Riboswitches are a newly discovered large family of structured RNA elements that are typically located at 5′ untranslated regions of messenger RNAs, and are composed of an aptamer domain and an expression platform. The aptamer domain recognizes and binds specifically to cellular metabolites, and the expression platform can either inhibit transcription elongation or block translation to regulate gene expression. Even though structural studies of ligand-bound riboswitches by X-ray crystallography and NMR spectroscopy have provided insights into detailed RNA/ligand recognition and interactions, the structure of ligand-free riboswitches remains poorly characterized. To gain greater insight into the mechanism of riboswitches’ functions as they transition from ligand-free to the ligand-bound forms, we have employed a variety of biochemical, biophysical, and computational techniques including small-angle X-ray scattering and NMR spectroscopy to characterize the ligand-free and ligand-bound forms of riboswitches. Our data reveal that ligand binding of the RNAs causes significant conformational change that may be important for its ability regulate gene expression.

150. Probing the molecular determinants of HIV alternative splicing: NMR and thermodynamic studies of UP1/ESS3

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Alternative splicing of the human immunodeficiency virus type-1 (HIV-1) genomic RNA is necessary to produce the complete viral protein complement, and aberrations in the splicing pattern impairs HIV-1 replication. The cellular protein, hnRNP A1 (A1), regulates splicing activity at several highly conserved 3′ alternative splice sites (ssA2, ssA3, and ssA7) by binding 5′-UAG-3′ motifs embedded within regions containing higher-order RNA structure. The physical determinants of A1/splice site recognition remain poorly defined in HIV-1; thus precluding a detailed understanding of the molecular basis of the splicing pattern. Here, the first 3D structure of an HIV-1 splicing regulatory RNA element, exon splicing silencer 3 (ESS3, located at ssA7), has been determined by solution 2H-edited NMR spectroscopy and restrained molecular dynamic simulations. ESS3 adopts a 27-nucleotide hairpin loop where the first 10 base pairs form an A-helical structure. The helix is interrupted by a pH sensitive A•C base pair that is conserved across several HIV-1 isolates. The seven nucleotide loop contains the high affinity A1 responsive 5′-UAGU-3′ epitope, and a proximal 5′-GAU-3′ motif. The NMR structure shows that the heptaloop adopts a preformed conformation stabilized by base stacking and non-canonical interactions. Significantly, the apex of the loop is quasi-symmetric where UA dinucleotide steps from the 5′-UAGU-3′ and 5′-GAU-3′ motifs stack on opposite sides of the hairpin - thereby providing a possible A1 binding platform. To further probe the physical determinants of high-affinity A1/ESS3 recognition, the thermodynamic profile ($\Delta G^{\circ}_{298K}$, $\Delta H^{\circ}_{298K}$, $\Delta S^{\circ}_{298K}$, and $K_c$) was measured via ITC for a C-terminal A1 deletion mutant (UP1). UP1 interacts with ESS3 via an enthalpically driven process - giving rise to a complex with nanomolar affinity. The ESS3 binding interface of UP1 was mapped via $^{15}$N-$^1$H HSQC titrations. The results show that the UP1/ESS3 binding interface is broad and involves regions not restricted to the beta-pleated sheet. Taken together, we present the first quantitative study of a host factor/HIV-1 splicing RNA element.
151. Optimizing research with NMR instrumentation

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Structure determination and dynamics characterization of biomolecules and their complexes by NMR spectroscopy is a field with many challenges. The measurement of poorly expressed proteins, very large systems and slow dynamics are just some of these challenges. Here we describe the large array of instruments, probeheads and, software that help to optimize research from the NMR study of biomolecules.

152. NMR tools for structural biology

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The NMR tools available for doing studies in structural biology are always improving. This talk will cover some of these recent developments and their applications.

153. Translational recoding by a chemo-mechanical retroviral mRNA switch

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For successful replication most retroviruses require translational recoding of the viral mRNA stop codon to maintain a precise ratio of structural (Gag) and enzymatic (Pol) proteins. Pol is expressed exclusively as a Gag-Pol fusion either by ribosomal frameshifting or by readthrough of the gag stop codon. While it is understood that the frequency of the recoding event is regulated by cis RNA motifs, no explanation is currently available for how the critical protein ratio is maintained. Our structure of the murine leukemia virus recoding signal shows that a protonation-induced conformational switch occurs in the RNA structure. The equilibrium is such that at physiological pH the active readthrough permissive conformation is populated at ~8%: a level that correlates with in vivo protein quantities. The RNA functions by a highly sensitive, chemo-mechanical coupling that ensures an optimal readthrough frequency. Similar observations for a frameshifting signal suggest that RNA structural transitions may have a general role in translational recoding.

Nanoparticle Metrology
Organizer: M. Zachariah

154. Intelligent design of Nanomaterial for drug delivery: Metrology challenges

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The exquisite control of matter at Nanoscale is leading to the discovery of novel phenomenon altering our daily lives. In medicine, these innovations are facilitating early diseases detection, better diagnostic, treatment, and device development to improve the quality of life. Many nanotechnology based therapies are already in clinical use for cancer and others are in advanced clinical and pre-clinical development.

This presentation will highlight the nuances in the chemical design of nanomaterial with appropriate size, surface characteristics and stability since these factors influence the biocompatibility, biodistribution, safety and efficacy of the formulations. Advances and current challenges in preclinical physico-chemical characterization of multifunctional nanomaterial will be presented. Resources available
Light scattering by particles offers a non-intrusive way to probe colloidal or aerosol systems, and it has a long and venerable history of such application. However, understanding and describing light scattering by particles can be difficult given the complex mathematical structure of the theory and the wide variety of particle shapes one encounters in nature. In this presentation I will show that a number of simplifying assumptions can be made or patterns can be discerned that allow for a fairly comprehensive description. A key feature of our approach is largely to abandon the scattering angle as the independent variable and use instead the dimensionless variable qR, where q is the scattering wave vector and R is the radius of the sphere. Then these patterns can be understood with straightforward and intuitive explanations often involving dimensional analysis. Spherical particles and fractal aggregates of all sizes will be considered and some of our principles will be extended to other shapes.

Complementary physical characterization methods in both fluid and ambient conditions were used to interrogate molecular adsorption onto gold nanoparticles (AuNPs) and the formation of AuNP clusters (AuNPCs). From the change of particle size in solution, the formation of AuNPCs and surface coatings can be monitored and evaluated quantitatively. For the purpose of characterizing AuNP-based platforms intended for applications in nanomedicine, AuNPs conjugated with thiolated polyethylene glycol (SH-PEG) were used as a model system. Dynamic light scattering (DLS) and asymmetric-flow field flow fractionation (AFFF) were used to characterize particle size and size distributions under relevant fluid conditions. For comparison, atomic force microscopy (AFM) and electrospray-differential mobility analysis (ES-DMA) offer static imaging and dry aerosol characterization, respectively. Combining the information derived from these physical-based methods provides a more comprehensive understanding of the model system than would be attainable from either method alone, thereby enabling analysis of the molecular conformation and adsorbed surface density for SH-PEG on the AuNP surface, and estimation of the degree of clustering and shelf life of AuNP based products in dispersed form.
157. **Intensity-Modulation Photoacoustic Spectroscopy for Optical Metrology of Aerosols and Nanoparticles**

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Photoacoustic spectroscopy is a powerful analytical tool for quantitative measurements of absorption coefficients of aerosols and nanoparticles. Recent developments in experimental techniques, methodology, and mathematical modeling have resulted in unprecedented levels of photoacoustic measurement sensitivity and fidelity. In this presentation, the performance metrics of a recently developed aerosol photoacoustic spectrometer are discussed and put in the context of other new advancements in the optical spectroscopy literature. As presently implemented, this spectrometer has a detection limit of $3.1 \times 10^{-9}$ W·cm$^{-1}$·Hz$^{-1/2}$ for gases and $1.5 \times 10^{-8}$ W·cm$^{-1}$·Hz$^{-1/2}$ for aerosol particles. A focus will be on instrument construction, calibration, uncertainty analysis, and common pitfalls encountered in experimental photoacoustics. Illustrations of this technique will be presented for measurement of 100, 150, and 200 nm black carbon aerosol particles.

158. **Elucidating architectures in bimetallic nanostructures**

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Pt-Ru nanoparticles of the same size and composition can be prepared in four different architectures: alloys, core-shell particles, mixtures of monometallic particles, and linked monometallic particles. Full structural and compositional characterization of the particles and catalysts requires multiple analytical techniques, including TEM-EDS, XRD, PDF, EXAFS, XANES and surface probe studies. These systems have been investigated for use in preferential oxidation of CO contaminants in hydrogen feeds (PROX) and for CO-tolerant hydrogen PEMFC anode electrocatalysts.

159. **Chemical and structural characterization of carbon nanotube surfaces**

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To utilize carbon nanotubes (CNTs) in various commercial and scientific applications, the graphene sheets that comprise CNT surfaces are often modified to tailor properties, such as dispersion. In this presentation, I will provide a critical review of the techniques used to explore the chemical and structural characteristics of CNTs modified by covalent surface modification strategies that involve the direct incorporation of specific elements as well as inorganic or organic functional groups into the graphene sidewalls. Using examples from the literature, I will discuss not only the popular techniques such as TEM, XPS, IR, and Raman spectroscopy but also more specialized techniques such as chemical derivatization, Boehm titrations, EELS, NEXAFS, TPD, and TGA.
The chemical or structural information provided by each technique is discussed, as well as their strengths and limitations. Particular emphasis is placed on XPS and the application of chemical derivatization methods used in conjunction with XPS to quantify functional groups on CNT surfaces.

160. **On-the-fly measurement of the length distribution and density of nanowires**

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We demonstrate that gas phase differential mobility separation enables one to classify diameter-selected nanowires by length. A by product of this work was the development of a theory to describe the behavior of nanowires undergoing Brownian rotation in an electric field, and provide a more rigorous interpretation of the experimental results. Experiments were conducted on the growth kinetics and length distribution of carbon nanotubes grown in the aerosol phase. By combining differential mobility separation with aerosol particle mass analysis we also demonstrate the ability to measure the density of nanowires on the fly.

**Medicinal Chemistry and Chemical Biology of Anticancer Agents**

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161. **The Preparation and Evaluation of Some Novel C-linked Carbohydrate Quinoline Hybrids**

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Novel C-linked carbohydrate based quinolines and tetrahydroquinolines have been synthesized via Povarov reactions between glycals and benzaline derivatives. Lead compounds in the quinoline series were shown to interact with both double-stranded and G-quadruplex forms of DNA and to selectively inhibit the growth of some leukemia cell lines. These studies and other recent studies directed towards the synthesis of bis-intercalators by a “double” Povarov reaction will be discussed.

162. **Synthesis and DNA binding of chiral oxazoline platinum (II) complexes: design of novel anti-cancer drugs**

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Although bioxazoline ligands of palladium and copper are widely used in asymmetric catalysis, platinum complexes bearing chiral oxazoline ligands have not been extensively explored. With the dual goals of studying the interaction of chiral platinum complexes with DNA and developing new anticancer agents, a series of platinum (II) complexes of the type Pt(biox)X containing C₅-symmetric bioxazoline ligands (R,R- or S,S-4,4'-R₂-2,2'-bioxazoline, R = -H, -Me, -iPr, -Bz; X = mono- or bidentate ligand) have been prepared and their reactions with mononucleotide and DNA have been investigated by a combination of NMR and computational (molecular dynamics) methods. Pt(biox)²⁺ complexes bind calf thymus DNA at comparable loadings compared with cisplatin and the geometry of Pt(biox)(oligonucleotide) complexes determined by molecular dynamics simulations maintains the expected square planar geometry about platinum.
163. NSAID Induction of the p75NTR Tumor Suppressor via the p38 MAPK Signal Transduction Pathway

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Chronic consumption of Non-Steroidal Anti-Inflammatory Drugs (NSAIDs) has been associated with a reduced incidence of bases and produce mutations that may eventually lead to transformation of cells and carcinogenesis. NSAIDs inhibit inflammation and therefore may reduce the incidence of carcinogenesis by preventing free radical transformation of cells. In parallel, specific NSAIDs induce p75NTR suppressor activity which manifests as apoptosis of prostate cancer. Pathologic inflammation can induce oxidative stress generating free radicals that damage and cause inhibition of cell migration in transformed cells. Hence, in post-transformed cells, NSAIDs may eliminate tumor cells through expression of p75NTR dependent apoptosis. In pathologic human prostate cancer tissues the p75NTR protein exhibits focal loss of expression which is lost with malignant progression of tissues. Significantly, loss of p75NTR protein expression occurs by loss of mRNA stability, however, the gene for p75NTR remains intact in the tumor cells. Treatment of tumor cells with aryl propionic NSAIDs promotes mRNA stability and re-expression of the p75NTR protein along with p75NTR dependent suppressor activity. Furthermore, the biochemical pathway by which these NSAIDs induce p75NTR appears to be independent of the COX pathway since COX null cells treated with NSAIDs retain the capability to re-express p75NTR protein. The p38 MAPK pathway appears central to the aryl propionic acid NSAID re-induction of p75NTR expression and associated suppressor activity in tumor cells. Aryl propionic NSAIDs induce phosphorylation of p38 MAPK downstream from MKK6 phosphorylating activity. Phosphorylation of p38 MAPK initiates a signal transduction cascade for subsequent phosphorylation of MK2 and MK3 leading to p75NTR mRNA stabilization, increased p75NTR protein levels and reduced cell survival. An opposite effect of the isoflavone, biochanin A, to antagonize NSAID induced phosphorylation of p38 MAPK inhibits p75NTR protein expression and increases cell survival. The ability of NSAIDs to induce phosphorylation of p38 MAPK dependent p75NTR expression and conversely biochanin A inhibition of p38 MAPK phosphorylation with consequent inhibition of p75NTR levels demonstrates the central role of the p38 MAPK pathway in aryl propionic NSAID induction of p75NTR expression. Functionally, p75NTR re-expression in prostate tumor cells reduces cell survival through G1 cell cycle arrest and induction of apoptosis consistent with its tumor suppressor activity. Significantly, expression of NSAID associated gene-1 (NAG-1) is also induced by aryl propionic acid NSAIDs through the p38 MAPK pathway downstream of p75NTR expression. In prostate cancer cells NAG-1 expression does not reduce cell survival, but rather, it inhibits cell migration. Hence, the NSAID induced NAG-1 expression and activity may form the basis of the metastasis suppressor activity of p75NTR expression with associated downstream NAG-1 expression in prostate tumor cells. In summary, aryl propionic NSAIDs induce phosphorylation of the p38 MAPK pathway which promotes mRNA stability and re-expression of p75NTR protein as well as downstream NAG-1 protein. Functionally, p75NTR expression forms the basis for tumor suppressor activity, whereas NAG-1 expression promotes metastasis suppressor activity in prostate tumor cells. These results provide a biochemical basis for NSAID associated reduced risk of prostate cancer.
164. Development of 2,3-disubstituted-1,4-naphthoquinone derivatives as potential therapeutic agents for the treatment of prostate cancer
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The quinone moiety is an valuable part of many biologically active natural products and their synthetic analogs. Natural and synthetic quinones exhibit a variety of biological activities, including anticancer activities. Quinonoid anti-cancer agents like doxorubicin, daunorubicin, mitoxantrone and mitomycin C have been used for many years in the treatment of various types of cancers, including solid tumors. These compounds act on various biological targets and/or pathways leading to cell death. In attempts to develop more cancer-selective quinonoid compounds as anticancer drugs, we have developed several 2,3-disubstituted 1,4-naphthoquinone derivatives for biological studies. We hereby present synthetic strategies for some novel imidonaphthoquinone and oxazolonaphthoquinone derivatives. In addition, their cytotoxicity studies on androgen independent, PC-3 and DU145, and androgen dependent LNCap prostate cancer cell lines will be presented.

165. Neuropeptide Y and its Y2 Receptors – Potential Targets in Neuroblastoma Therapy
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Neuropeptide Y (NPY) is a sympathetic neurotransmitter, acting via multiple G protein-coupled receptors (Y1-Y5R). Neuroblastomas, the pediatric tumors of sympathetic origin, release NPY, which results in its elevated plasma levels in patients with advanced disease and a poor clinical outcome. We have shown that NPY is an endogenous growth factor for neuroblastoma, which stimulates tumor cell proliferation and tumor vascularization. Both of these processes are mediated by its Y2Rs, suggesting that blocking NPY/Y2R autocrine loop may lead to inhibition of the tumor growth. Indeed, in neuroblastoma cells, Y2R antagonist (BIIE0246) prevented activation of p44/42 MAPK induced by endogenous NPY, which resulted in decreased proliferation and induction of Bim-mediated apoptosis. Similar growth-inhibitory effects were achieved with NPY siRNA and Y2R siRNA. In vivo, Y2R antagonist significantly inhibited growth of neuroblastoma xenografts, which was associated with decreased activation of p44/42 MAPK, as well as reduced proliferation (Ki67) and increased apoptosis (TUNEL). The Y2R antagonist also exerted an anti-angiogenic effect. In vitro, it reduced the proliferation of endothelial cells induced by neuroblastoma-conditioned media. Consequently, the Y2R antagonists-treated xenografts had decreased vascularization and a high degree of focal fibrosis. In human neuroblastoma tissues, the expression of Y2R was observed in both tumor and endothelial cells, while NPY was predominantly expressed in neuroblastoma cells. Importantly, both NPY and its Y2Rs were present in vast majority of human neuroblastoma samples, proving their value as universal thera-
peutic targets. This is in contrast to some other molecules implicated in neuroblastoma, such as ALK, inhibitors of which affect only a small subset of neuroblastoma tumors. Notably, the Y2R antagonist used in this study is known to be extremely unstable, suggesting that the efficiency of this treatment can be further enhanced by designing more potent Y2R antagonists. In summary, Y2R is a promising new target for neuroblastoma therapy affecting both cancer cells and tumor vasculature.

166. Can anti-angiogenic tyrosine kinase inhibitors enhance cancer vaccines?

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Cancer vaccines are a novel, highly attractive therapeutic modality that may circumvent the drug resistance that underlies treatment failure in advanced cancers. However, their activity is limited by intricate networks of immune tolerance, and established burdens of disease. Our group leads the immunotherapy field in strategically partnering cancer therapeutics with vaccination to capitalize on the cytoreductive potential of cancer drugs, and their ability to impinge on immunoregulatory networks to favor tumor immunity. We have used the paired FVB/N—neu N mouse model of HER-2+ breast tumors (no immune tolerance/immune tolerance) to investigate mechanisms of synergy and antagonism between distinct drugs and tumor vaccines. HER-2-targeted, granulocyte-macrophage colony-stimulating factor (GM-CSF)-secreting vaccination alone is curative in tumor-bearing FVB/N mice, but ineffective in neu-N mice with tumors. Sequencing the vaccine with low dose Cyclophosphamide (CY) and Doxorubicin (DOX) cures about 30% of neu-N mice, in part by abrogating the influence of CD4+CD25+ regulatory T cells (Treg). We have completed a 28 patient clinical study investigating a human HER-2+ GM-CSF-secreting vaccine with a range of low dose CY and DOX, and demonstrated that the vaccine sequenced with 200 mg/m² CY and 35 mg/m² DOX is well-tolerated, and optimizes CD4+ T cell-dependent immunity. Because there was no evidence of objective tumor regression, immune-inhibitory pathways at the tumor site likely blunt the immune response. Accordingly, we are developing a multi-targeted, chemotherapy-modulated vaccination strategy incorporating multi-kinase inhibitors that target both the tumor cells, and other distinct cellular components within the tumor microenvironment, thereby removing the roadblock to infiltrating immune effectors. We recently discovered a novel immune-modulating activity for the VEGFR2-specific monoclonal antibody DC101. DC101 alone cures tumor-bearing FVB/N mice through both anti-angiogenic and immune effects. In contrast, DC101 alone only controls tumor growth in neu-N mice, and only by inhibiting the vasculature during active treatment. Importantly, adding DC101 to chemotherapy-modulated vaccination in tolerant neu-N mice increases the vaccine-mediated cure rate by 4-fold. It remains unclear if this immune activity is related to the specificity of DC101 for endothelial cells, or requires its antibody structure. We have extended these studies to explore the activity of the small molecule multi-kinase inhibitors sorafenib and sunitinib, both of which have been developed as anti-angiogenic therapies. Sunitinib 40 mg/kg daily by gavage is as effective as HER-2-targeted vaccination in non-tolerant FVB/N mice, resulting in 100% tumor rejection. In contrast, sorafenib 30 mg/kg by gavage effectively initially causes tumor regression, but tumors ultimately stabilize in size and are not rejected. The addition of vaccine to either of these drugs in non-tolerant mice accelerates vaccine-mediated rejection, and does not impact the magnitude of interferon-γ-secreting CD8+ T cells induced. In tolerant neu-N mice, vaccine alone is completely ineffective in delaying tumor outgrowth, and sorafenib 30 mg/kg daily only slightly delays tumor outgrowth. Sunitinib 40 mg/kg daily restricts tumor growth, resulting in the stabilization of small tumors. Additional data suggest that the activity of these drugs is in part T cell-dependent, and likely affects other innate immune effectors as well. These studies will ultimately select the most active MKI to incorporate into a clinical trial of MKI-chemotherapy-modulated vaccination in patients with metastatic breast cancer.
Monoclonal antibodies (MAB) have become a crucial therapeutic agent in a number of anti-cancer treatments. Over 20 have been approved by the FDA for clinical use while several hundred are now in clinical trials. MABs introduced to the human body have low biological potency and thus to be effective, large doses (several hundred milligrams) are necessary. Most treatments are presently initiated through a lengthy intravenous route, but a home or clinical treatment is presently desired for the purpose of convenience which requires a subcutaneous dosing regimen. This procedure poses a restriction of the amount of sample which can be injected (<1.5 mL), and high concentration is thus necessary to be biologically effective. Unfortunately, certain MABs at increased volume fractions exhibit an undesirable increase of viscosity (>50 cP) which makes the injection process more difficult or impossible due to the restricted flow of the MABs (Fig. 1).

It has been proposed that a dramatic viscosity increase of some MABs at high concentrations is not only due to volume exclusion effects, but also the formation of different types of higher-order liquid structures at the nano-length scale that are dictated by MAB self-associations. Our group has shown that even small alterations in the primary structure of a MAB and the buffer conditions can substantially alter the resulting viscosity. Therefore, it is of immense importance to understand the nature of these self-associations for each MAB in a multiple different buffer conditions at equilibrium.

References


167. Small-Angle neutron scattering and rheological characterization of monoclonal antibodies at high concentrations

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Monoclonal antibodies (MAB) have become a crucial therapeutic agent in a number of anti-cancer treatments. Over 20 have been approved by the FDA for clinical use while several hundred are now in clinical trials. MABs introduced to the human body have low biological potency and thus to be effective, large doses (several hundred milligrams) are necessary. Most treatments are presently initiated through a lengthy intravenous route, but a home or clinical treatment is presently desired for the purpose of convenience which requires a subcutaneous dosing regimen. This procedure poses a restriction of the amount of sample which can be injected (<1.5 mL), and high concentration is thus necessary to be biologically effective. Unfortunately, certain MABs at increased volume fractions exhibit an undesirable increase of viscosity (>50 cP) which makes the injection process more difficult or impossible due to the restricted flow of the MABs (Fig. 1).

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Small-angle neutron scattering (SANS) can probe not only the size and shape of proteins in solution, but also their self-interactions. Accordingly, equilibrium SANS data on several MAbs at differing concentrations and buffer conditions were collected and analyzed. It was found that neither the concentration nor the temperature has an effect on the individual MAb form factor. Additionally, pH and surfactant free conditions do not lead to any observable structural changes. In contrast, the SANS data indicate the inter-particle structure factors, and accordingly the protein-protein interactions, of the MAbs differ tremendously depending on the conditions. A more detailed analysis of the inter-particle structure factors demonstrates that small clusters are forming in the more concentrated samples. This observation is consistent with the proposal that the significant increase in viscosity observed for a number of MAbs is related to the crowding of higher-order structures formed by highly concentrated MAbs.

168. Cytotoxicity studies of selected emetine dithiocarbamate ester derivatives in androgen-positive prostate cancer LNCaP cells

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We have previously reported the synthesis and characterization of a 12-member library of emetine dithiocarbamate ester derivatives. Preliminary evaluation of these compounds on two androgen-independent prostate cancer cell lines has also been presented. In the current study, the concentration and time dependent cytotoxicity studies of selected emetine dithiocarbamate ester derivatives in androgen-positive prostate cancer LNCap cells is presented. The potency of the selected derivatives on the androgen-positive LNCaP compared to the hormone-refractory PC3 and DU145 cells is discussed.
169. Photochemical Regulation of Oligonucleotide Function with Applications to Biological Systems

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Recently, we developed photocaged phosphoramidites for the synthesis of light-activated DNA. We have applied this methodology to the engineering of mammalian cells and multicellular model organisms to respond to light with the activation or deactivation of gene function. The developed biological light-switches have vast applications in the investigation of gene function and the study of developmental processes. Light represents an excellent control element since it can be regulated with high spatial and temporal precision. Here, selected examples of recent developments will be presented, including: a) light-regulation of DNA:DNA hybridization enabling photochemical control of DNA polymerization and enzymatic activity, and b) light-regulation of DNA:RNA hybridization allowing for photochemical control of antisense activity and gene function in mammalian cell culture and in aquatic embryos.

170. Synthesis of 2'-O-aminooxymethyl ribonucleosides and their use in the labeling of DNA and RNA sequences

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A novel and convenient approach to the preparation of 2'-O-aminooxymethyl ribonucleosides is presented. This synthetic approach is based on the 2'-thioacetalization of commercially available (3',5')-disilylated, optionally \(N\)-protected, ribonucleosides followed by the consecutive transformation of their 2'-methylthiomethyl ether derivatives to their 2'-chloromethyl ether intermediates and 2'-phthalimidoxyethyl ether derivatives. Reaction of these 2'-O-phthalimidoxyethylated ribonucleosides with \(\text{NH}_2\text{F}\) in MeOH resulted in their concomitant desilylation and unprecedented dephthalimidation to give the desired 2'-O-aminooxymethyl ribonucleosides. Oximation of aldehydes or ketones by treatment with 2'-O-aminooxymethyl ribonucleosides led to the formation of temporary or permanent ribonucleoside 2'-conjugates, respectively, in good yields. Although temporary conjugates are stable compounds, they are unstable when exposed to 0.5 M tetra-n-butyrammonium fluoride (TBAF) in THF. Under these conditions, a fluoride-mediated cleavage of the iminoether function of each temporary conjugate occurs and results in the formation of the native ribonucleoside along with the release of an innocuous nitrile side product. Thus, these findings support an innovative strategy for the design of new 2'-hydroxy protecting groups in the synthesis of native or modified RNA
sequences. Given that permanent ribonucleoside 2'-conjugates are stable to TBAF treatments, the versatility of 2'-O-aminoxyomethyl ribonucleosides in the preparation of ribonucleoside 2'-conjugates with various functional groups allows permanent or temporary labeling of DNA and/or RNA sequences through the use of appropriate phosphoramidite derivatives of these conjugates.

171. Consequences of positively charged thiophosphate protecting groups on the cellular uptake of thermolytic oligonucleotide prodrugs.

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The therapeutic application of synthetic DNA/RNA oligonucleotides (ODNs) to silence gene expression through an antisense or an RNA interference pathway is an attractive approach to the treatment of infectious diseases and various cancers. However, the polyanionic nature of ODNs has impeded their efficient delivery through cellular membranes. In order to alleviate this problem, the heat-sensitive groups for masking the negatively charged thiophosphate functions of bioactive phosphorothioated (PS) ODN have been developed in our laboratory. The unique feature of these thermosensitive PS-ODN prodrugs (pro-ODNs) is their temperature-dependent conversion to bioactive PS-ODN drugs. Indeed, the kinetics of pro-ODN conversion to PS-ODN drugs at 37 °C depends on the nature of the thermosensitive thiophosphate masking group being used. For example, the heat-sensitive 2-(N-formyl-N-methyl)aminoethyl (FMA) group for thiophosphate protection of pro-ODNs were found to impart immunoprotection to mice against Leishmania and Tacaribe virus after a post-infection time of 72 h. The objectives of the current research effort are to optimize the solubility and cellular uptake properties of FMA-masked PS ODN prodrugs. The synthesis of 5'-fluorescently labeled FMA pro-ODNs (15-mers) carrying a limited number of either negatively charged thiophosphate diesters or positively charged 3-(dimethylamino)prop-1-yl thiophosphate triesters was performed in order to increase the solubility of pro-ODNs and assess their cellular uptake in a Vero cell line. A systematic cellular uptake study using flow cytometry was performed and indicated that FMA pro-ODN carrying four positive charges led to vastly superior (ca. 20-fold) cellular uptake properties than those of PS-ODN diesters. Furthermore, confocal microscopy analysis indicated that the positively charged FMA pro-ODNs were taken up by live Vero cells and were found to gradually move to the nuclei of these cells over a period of 24 h. Currently, studies are underway to further evaluate the parameters controlling cellular uptake of these positively charged pro-ODNs in Vero and other cell lines.

172. Molecular mechanics- and quantum mechanical-assisted conformational analysis of five-membered rings: PSEUROT 2011

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In contrast to six-membered rings, where there is a strong preference for chair conformations, the five-membered rings of nucleosides and nucleotides can exist in a variety of conformations depending on which of the ring atoms are puckered above and below the general ring plane. For five-membered rings there is a family of twenty possible conformations (the ‘north-south’ formalism), and which conformer(s) dominate the equilibrium is generally established using 1H-1H coupling constants derived from NMR spectroscopy and the PSEUROT program. The conformational analysis of novel nucleos(t)ides is complicated by the fact that certain needed structural parameters may not be present in the PSEUROT database. This talk will focus on comparing the relative merits of molecular mechanics (AMBER)- and quantum mechanical (6-31G and higher basis sets)-based methods for obtaining the PSEUROT parameters, with an emphasis on how the proper selection of an atomic point charge calculation method makes AMBER competitive with ab initio methods.
173. Noncanonical role of PCNA ubiquitylation in eukaryotic translesion synthesis

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Translesion synthesis (TLS), a mechanism utilized by cells to synthesize past DNA lesion, is evolutionarily conserved in organisms from prokaryotes to eukaryotes. Ubiquitylation of proliferating cell nuclear antigen (PCNA) plays an important role in eukaryotic TLS. The molecular details of how ubiquitylated PCNA regulates TLS are poorly understood. To facilitate biochemical investigation of TLS, we developed a chemical approach for PCNA ubiquitylation. The chemically ubiquitylated PCNA is functionally equivalent to the native ubiquitylated PCNA in effecting polymerase switch. We also demonstrated the strict requirement of PCNA ubiquitylation for polymerase exchange between Polδ and Polη. Moreover, we probed the effect of the site of ubiquitylation by preparing chemically ubiquitylated PCNAs that differ only in the position of modification. Our study revealed a high degree of mobility of ubiquitin moiety on PCNA. Another important aspect of ubiquitylation in TLS is how the specialized DNA polymerase is recruited to the lesion site. The ubiquitin binding zinc finger (UBZ) domain in the C-terminal portion of Polη is known for its ability in binding ubiquitin. However, the interaction between Polη UBZ and ubiquitin was shown to be surprisingly low with a previously reported Kd of approximately 80 micromolar. This low-affinity binding between Polη UBZ and ubiquitin has been difficult to reconcile with its essential role in TLS revealed by genetic and cell biology studies. Using quantitative SPR binding assay, we revealed that compared to the isolated UBZ the C-terminal portion of Polη binds ubiquitin with a much higher affinity and with a distinct binding kinetics. This observation raised the possibility that the C-terminal Polη binds ubiquitin in a novel mode to afford higher affinity interaction. Our findings have broader implication in understanding the generally weak interaction between known ubiquitin-binding domains and ubiquitin. This work was supported by a grant to Z.Z. from National Science Foundation (MCB0953764).

**174. Psoralen photochemistry illuminates cellular pathways of DNA interstrand crosslink repair**

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Interstrand cross-links (ICLs) are absolute blocks to transcription and replication and can provoke genomic instability and cell death. The pronounced toxicity of ICLs underlies the widespread use of DNA crosslinking compounds in cancer chemotherapy. However, despite the lengthy clinical history, ICL repair is poorly understood.

We have developed a novel experimental strategy that exploits the photochemistry of psoralens. ICLs are introduced into defined subnuclear regions by laser localized photoactivation of antigen tagged psoralen, after which ICL repair and the recruitment of repair proteins can be monitored by immunofluorescence confocal microscopy. This permits the visualization and quantification of ICL repair. Protein recruitment can be followed immediately after ICL formation, in real time in live cells, which is not possible with other approaches.

Fanconi Anemia (FA) proteins are known to be recruited to ICL blocked replication forks, while their contribution to DNA repair in other phases of the cell cycle remains obscure. We found that FA core complex proteins FancM (3 min) and FancE/FancF (5 min) recruited exclusively in S phase to laser localized ICLs. However, FancD2 localized (10-15 min) at all phases of the cell cycle, in a FA core complex dependent fashion. Thus, core complex function, but not necessarily colocalization, was required for FancD2 recruitment.

Recently, the FancD2 Associated Nuclease (FAN-1) has been reported to require ubiquitinated FancD2 to form foci in S phase cells upon treatment of cells with slowly acting ICL-inducing compounds, such as mitomycin C. However, we found that FAN-1 localizes immediately (10sec) to ICL sites independently of FancD2 and displays a second phase of recruitment (10min), which is dependent on its ubiquitinated FancD2 binding motif (UBZ). Thus FAN-1 may function in two separate pathways.

**175. Mutation spectrum and pattern of p53 mutagenesis due to B[a]P radical cations in a yeast based reporter system**

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Benzo[a]pyrene is an ubiquitous air pollutant released as a result of fossil fuel combustion and cigarette smoke. B[a]P is a major carcinogen responsible for lung cancer. B[a]P is metabolically activated in vivo to mutagenic metabolites that makes its exposure a risk factor in human lung cancer. Out of the three principle routes of activation of B[a]P, CYP450 mediated formation of the ultimate carcinogen (+)-anti-BPDE and its mutagenesis has been well documented and studied. Mutagenic effect of B[a]P radical cations formed by action of CYP peroxidases has not been studied in p53 oncogene. The tumor suppressor gene p53 is commonly mutated in lung cancer. We have used a yeast based reporter system to study p53 mutagenesis due to B[a]P radical cations generated *in situ*. Since B[a]P radical cations are short-lived species, they were generated *in situ* enzymatically using HRP, CuOOH as HRP substrate and 50uM B[a]P as the electron donor. Mutagenic effects of *in situ* generated radical cation were compared with B[a]P-7, 8 dione (250nM). B[a]P radical cations were not as mutagenic compared to (+)-anti-BPDE or ROS generated due to B[a]P 7,8-dione in the yeast assay. The frequency of mutation increased when the Apn1 gene was knocked out suggesting that the mutations maybe caused due to formation of AP sites. G>T mutations are the signature mutation type in lung
cancer and activated PAH-metabolites may cause G>T transversions. We found that about 12% of the mutations due to B[a]P radical cations are G>T transversions which is lesser than the % seen with BPDE or BP-7, 8 dione.

**Biochemistry Poster Session II**  
Organizer: P. Deshong

### 176. Expression and purification of the protease and the receptor binding domains of Botulinum neurotoxin A

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Botulinum neurotoxin A (BoNT/A) is the most toxic substance known to man because of its very tight binding to the receptors and highly specific protease activity. The neurotoxin has broad applications in the study of neuroscience and in treatments of neurological diseases. The tripartite neurotoxin consists of three domains for proteolysis (light chain), membrane translocation and receptor binding. The cDNAs encoding the protease domain (LC) and the receptor binding domain (RBD) of BoNT/A were synthesized using booster-touchdown PCR from codon-optimized oligonucleotides. The cDNAs were subcloned into the TOPO vector and sequence errors were corrected by site-directed mutagenesis. BoNT/A LC and BoNT/A RBD with 6xHis were expressed as fusion proteins with small ubiquitin modifier 1(SUMO1) in E. coli BL21(DE3). The expression conditions were optimized to maximize the yields. Both SUMO-BoNT/A LC and SUMO-BoNT/A RBD were purified using affinity chromatography on Ni-NTA. The overall yields were 4 mg and 0.8 mg per 100 ml culture for SUMO-BoNT/A LC(1-425) and SUMO-BoNT/A RBD, respectively. The expression and purification of individual domains facilitate the study of the receptor binding and protease activity, and the development of therapeutics.

### 177. Insertion of selenocysteine into the redox-active cysteine-x-x-cysteine motif of the flavoprotein augmenter of liver regeneration

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Augmenter of liver regeneration (ALR) is a mitochondrial enzyme that aids disulfide bond insertion into reduced unfolded proteins. ALR employs two active site cysteines in conjunction with a flavin prosthetic group to facilitate the formation of disulfide bonds. The reactive cysteines are part of a cysteine-x-x-cysteine redox motif (where x stands for any amino acid). In order to study the catalytic mechanism of ALR we have modified the redox potential by introducing a selenocysteine in place of a cysteine within the cysteine-x-x-cysteine motif. Selenocysteine is a naturally occurring amino acid whose pK_a and redox potential are lower than that of cysteine. Hence, while this mutation is not expected to introduce structural changes,
the redox potential of the modified ALR is likely to be substantially lower than that of the wild type protein.

Selenocysteine was incorporated into ALR by manipulating the *Escherichia coli* selenium incorporation machinery. The UV-VIS absorbance spectrum of the cysteine-x-x-selenocysteine containing enzyme is shifted from 456 to 450 nm, indicating a slightly different environment for the flavin cofactor. Measurements of catalytic activity and the behavior of selenium-incorporated ALR will be reported.

178. Turnip Mosaic Virus Genome-Linked Protein (VPg) Inhibits Pokeweed Antiviral Protein (PAP)-Mediated Depurination of RNA

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Pokeweed antiviral protein (PAP) [Figure 1] from *Phytolacca americana* [Figure 2] is a ribosome inactivating protein (RIP) and is an RNA N'-glycosidase that removes specific purine residues from the sarcin/ricin (S/R) loop of large rRNA, arresting protein synthesis at the translocation step. PAP is a cap-binding protein, and it was suggested that it inhibits translation of RNA by binding to the 5’ m7G cap structure of eukaryotic mRNA, and depurinating the mRNA at sites downstream of the cap structure. PAP is a potent antiviral agent against many plant, animal, and human viruses. Depurination of capped viral RNA may be the primary mechanism for PAP’s antiviral activity. However, the above mechanism does not clarify the inhibitory effect of PAP on the replication of uncapped viruses. To elucidate the mechanism of RNA depurination, and to understand how PAP recognizes and targets various RNAs, the interactions between PAP and Turnip mosaic virus (TuMV) genome linked protein (VPg) were investigated. VPg is important in the initiation of protein synthesis, functioning as a cap analog. VPg stimulates the *in vitro* translation of uncapped IRES-containing RNA and inhibits capped RNA translation in wheat germ extracts. In this work, fluorescence spectroscopy and HPLC techniques were used to quantitatively describe PAP-VPg interactions. PAP interacts strongly with VPg, thus the effect of VPg on the PAP catalyzed depurination of several different RNA molecules was determined to investigate whether VPg binding to PAP influences selectivity of depurination. PAP binds to and depurinates both m7GpppG-capped and uncapped S/R oligo nucleotide and TEV RNAs, supporting previous conclusions that the cap structure is not the only determinant for PAP depurination of RNA. VPg decreases depurination of the above capped and uncapped RNAs and competes with TEV RNA for PAP binding. VPg may confer an evolutionary advantage by suppressing one of the defense mechanisms of the plant. Depurination inhibition of PAP by VPg also suggests the possible use of this protein against cytotoxic activity of RIPS and inhibition of their biological potency.
179. To develop alternative therapeutic approaches to the treatment of opportunistic infections

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Opportunistic pathogen *Burkholderia cepacia* is known to produce a family of 4-hydroxy-2-alkyl quinoline (HHQ) molecules involved in quorum sensing. Opportunistic infections are caused by bacteria in people with compromised immune systems such as people with HIV, cystic fibrosis, and older people. In nature, these bacteria interact via a shared communication system called quinoline quorum sensing (QQS). This quinoline quorum sensing has been shown to influence bacterial growth and gene expression. Understanding the biochemistry behind the synthesis of these QQS molecules will aid in the development of alternative therapeutic approaches towards the diagnosis and treatment of opportunistic infections. *Burkholderia* species produce mostly 2,3 unsaturated alkyl sidechains which is in contrast to other opportunistic pathogens such as *Pseudomonas* that have a high proportion of saturated alkyl sidechains. In our studies we will show that this unsaturation is a result of the *hmqF* gene which shows similarities to nonribosomal peptide synthetases, composed of three individual domains, an ATP ligase, a CoA dehydrogenase domain, and phosphopantetheine (pPant) attachment site or acyl carrier protein. We have observed by Fourier transform mass spectrometry (< 5 ppm) that the ATP ligase selectively activates the fatty acids as an AMP ester. The fatty acid selectivity of the ATP ligase domain was studied for fatty acids starting from hexanoic acid (C6) through myristic acid (C16). The ATP ligase was selective from hexanoic acid through lauric acid as observed by ATP-PPi exchange assay and mass spectrometry. The AMP ester was then loaded to the pPant arm of the ACP domain as observed by increased mass of the loaded ACP domain via mass spectrometry. The CoA dehydrogenase will then selectively desaturates the 2,3 bond to give an alpha-beta unsaturated thioester intermediate which will be monitored by pPant fragmentation mass spectrometry.

180. Testing the biochemical mechanism for the activation of apoptosis by the mitochondrial enzyme cytochrome c heme lyase (CCHL)

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Apoptosis (programmed cell death) is essential for normal animal development and for preventing cancer by eliminating at-risk cells. Apoptosis requires caspase enzymes that are kept inactivated in living cells by binding to IAP (inhibitor of apoptosis) proteins. Certain pro-apoptosis proteins, such as SMAC/DIABLO, trigger apoptosis when released from the mitochondria. These proteins bind IAPs to de-inhibit caspases. Recently, CCHL (cytochrome c heme lyase), the major cytochrome c biogen-
esis component in the mitochondrial intermembrane space, was implicated as a novel mitochondrial caspase activator. This project tests if CCHL physically binds IAPs. A yeast homologue of CCHL fused to a His\textsubscript{6} tag (His\textsubscript{6}-CCHL) and a fragment (BIR2 domain) of the human IAP homologue XIAP fused to glutathione-S-transferase (GST-XIAP) were expressed separately in \textit{Escherichia coli}. The expressed GST-XIAP was bound to a glutathione column (via GST fusion) by loading the induced cell lysate. Lysate from induced cells overproducing His\textsubscript{6}-CCHL was then loaded onto the column followed by extensive washing. SDS-PAGE (sodium dodecylsulfate polyacrylamide gel electrophoresis) of protein purification samples and subsequent Western blotting using anti-His\textsubscript{6} antibody revealed that His\textsubscript{6}-CCHL coincides with glutathione-based column elution of GST-XIAP. Moreover, control experiments showed no binding of CCHL to the glutathione column in the absence of GST-XIAP. These results indicate that CCHL can bind to IAPs. The binding interaction of human XIAP with the human CCHL homologue is currently being investigated. In the near future, the functionality of the binding interaction will also be assessed by testing the ability of CCHL to activate an XIAP-inhibited caspase in a fluorometric caspase assay.

181. Regulating multimeric enzymes by engineering controllable self-associating inhibitor proteins

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Many biological processes are controlled by protein self-association. Examples include the assembly of filaments from tubulin and the triggering of signals by dimerization of membrane receptors. We developed a method to experimentally control protein-self association using the DNA binding protein HAP1. The DNA-binding region (DBR) of HAP1 is monomeric in solution but binds cooperatively as a dimer to DNA containing the HAP1 binding site sequence. Recombinant DNA methods were used to fuse a 17 kDa DBR of HAP1 to the 43 kDa maltose binding protein (MBP). Gel filtration chromatography showed that the MBP-HAP1 fusion was monomeric. Adding HAP1 binding site DNA caused the MBP-HAP1 fusion to elute earlier as a much larger complex. Calculations based on the absorbances of eluted free and bound protein and DNA indicated a minimum 2:1 stoichiometry for MBP-HAP1:DNA in the complex. This demonstrated that DNA can control the self-association of HAP1 fusion proteins. The method is now being used to probe the regulation of a pro-apoptotic caspase. Caspases are multimeric enzymes that contain 2 active sites per protein. In cells, caspases are inhibited by IAP (inhibitor of apoptosis) proteins. The HAP1 DBR was fused to a monomeric fragment of the IAP protein DIAP1. This IAP-HAP1 fusion is being tested in a fluorometric caspase assay to determine if self-associating the IAP leads to more efficient and enhanced inhibition of the multimeric caspase. In addition to providing insight into the chemistry of apoptosis regulation, the results could aid in designing new strategies to regulate other multimeric enzymes.

182. Elasticity of Intrinsically Disordered Nebulin Modules

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The elasticity of native full length nebulin, demonstrated recently via atomic force microscopy with site-specific antibody pairs as force handles (Langmuir, 2009, 25, 7496), suggests that in the thin filaments, nebulin is stretched to cope with the actin length and imposes significant force and influences the functions of the underlying actins. This pre-stressed mechanical state of thin filaments may have important implications for the role of nebulin as a length ruler and as a regulator of actomyosin interaction. The structural basis of nebulin elasticity remains open. We report here the structural
characterization of modules from the super-repeat and single repeat regions by a combination of circular dichroism (CD), NMR, SAXS, AFM, structural predictions and steered molecular dynamics simulations. In aqueous solutions of common buffers, these modules are intrinsically disordered, but are poised to form alpha-helices, especially in the presence of trifluoroethanol. SAXS analysis of a four-module construct indicates an elongated structure with a radius of gyration of 3.6 nm and, as modeled with DAMMIN, shows a contour length of ~15 nm. Interestingly, this extended structure is also evident in a small population of the structural models as predicted by ROSETTA++. AFM images of the modules on an inert surface are predominantly compact with an average height of ~2.5 nm, consistent with the bulk of the ROSETTA predictions. These structural ensembles of compact and extended structures are significantly shorter than what it would take for nebulin modules to wrap around the perimeter of actin filaments (~6 nm per module). We propose that nebulin modules’ disorder-order transition of alpha helices, contributes to its elasticity and how nebulin juxtapositions itself onto the actin to form a pre-stressed thin filaments in the muscle sarcomere.

183. Measuring of the release of DNA subsites from the DNA-IHF complex.

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IHF (Integration Host Factor) is member of the DNABII family (necessary for chromosome bending) of DNA-binding proteins. It helps to maintain DNA supercoiling and condensation. It also plays an architectural role by bending DNA and this bending is important for transcriptional regulation, DNA replication and in DNA condensation: these processes require DNA bending to bring two far DNA sequences nearby.

The subunits of IHF are IHFa and IHFβ. Each subunit has 3 α helices and 4 β strands. IHF binds DNA with substantial sequence specificity but identifies its related sequences exclusively via indirect read-out. The IHF binding site has 3 subsites, those are A-tract i.e. 5’-AAAATAA-3’, 5’- TATCAA-3’ which is the center region and 5’-TTR-3’, where R is A or G, it is located 4 base pair in the 3’ direction from the former. IHF creates a U-turn in DNA by creating two kinks flanking the center of the recognition sequence; these kinks allow the DNA to be folded down the flanks of IHF, designated the TTG and A-tract flanks.

The objective of finding which arm is let loose easily and which is bound more tightly is obtained by restriction digestion with different enzymes and finding out the rate of cleavage in presence and absence of IHF. The IHF binding site allows placement of restriction sites in each subsites. The relative rates of cleavage with respect to a control substrate should reflect the relative release frequencies of the subsites. This restriction digestion is similar to the assay by Polach and Widom. They used this assay to show that nucleosomes are dynamic structures transiently exposing regions of their DNA and, thus, giving access of the target sites to regulatory proteins.

Restriction digestion assay reveals that A-tract is more accessible to restriction enzymes than other two subsites. This suggests that A-tract arm release more frequently than 5’-TTR-3’ arm.
184. Using the Functional Amino Acid Navigator to Understand Differences Between Substrate and Allosteric Effector Binding

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The purpose of the Functional Amino Acid Navigator (FAN) (http://www.palenchar-tools.org/FANindex.html) is to create a database that captures information about how enzymes function with respect to interacting with small molecules and critical amino acids involved in catalysis, and then use that database to address questions related to how enzymes function and genome annotation. FAN will give a detailed picture of enzyme interactions with small molecules at the atomic level. We have used the data contained in FAN to determine if allosteric effector binding sites are different than substrate binding sites. We have found that there are differences in the amino acid side chains that interact with the allosteric effectors and substrates. Furthermore, using BLAST and KEGG assignments of enzymes, we have studied the conservation of amino acids involved in substrate and allosteric effector binding, and we have found that amino acids involved in binding allosteric effectors are less likely to be evolutionarily conserved. Determining whether this is related to the evolutionary flexibility of regulatory control mechanisms or is related to the way in which enzymes are grouped by enzyme commission numbers will require further work.

185. 77Se as a Probe of Methionine's Role in Protein-Protein and Protein-Ligand Interactions

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Methionine has an important role in ligand and protein recognition by virtue of the high polarizability of the thioether sulfur in its highly flexible side chain. In addition to its role in recognition processes between nonpolar protein interfaces, methionine also contributes to antioxidative defense by scavenging reactive oxygen species. However, the conversion of thioether to sulfoxide by oxidation may result in loss of the protein's biological function and is directly linked to longevity and neurodegenerative diseases such as Alzheimer.

We probe the role of methionine in recognition and binding of proteins and ligands by recording its properties in different protein microenvironments. Since sulfur's only NMR sensitive nuclei, 33S, cannot be used to study macromolecules due to its low sensitivity, we use selenium as a surrogate for sulfur. We developed a general method to enrich proteins with 77Se by raising the selenium-to-sulfur ratios in the E. coli cells’ growth media. The detection of selenomethionine in different protein environments is described.

186. Maximum incorporation of selenium in E. coli cells for NMR spectroscopy

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Selenoproteins contain the rare amino acid selenocysteine. Selenocysteine is predominantly found in enzyme active sites where it provides high chemical reactivity and specificity, most often in redox regulation. In mammals, selenoproteins contribute to chemopreventive, anti-inflammatory, antiviral and antioxidative defense. Among the twenty-five human selenoproteins, are the important redox enzymes thioredoxin reductase (TrxR), selenoprotein P (SelP), and glutathione peroxidase (GP).
The production of selenoproteins is challenging due to the inherent inefficiency of selenium incorporation. Hence, their limited availability complicates their structural and functional characterization. We have developed a general method to enrich proteins with selenium by raising the selenium-to-sulfur ratios in the E. coli cells’ growth media. As may be expected, selenium toxicity impedes cell growth and protein expression. We have screened the growth conditions and ratio of sulfur/selenium in the media to obtain the desired yield vs. incorporation ratio. The method we have developed, using a ratio of 9:1 selenium to sulfur in the growth media, results in a substitution ratio of 70% selenium to sulfur and the yield is about ½ lower than that in a sulfur media. This method has been tested for several proteins and similar to the specific incorporation method discussed above is both robust and fully compatible with additional partial and uniform isotopic enrichment of recombinant selenoproteins with $^{77}$Se, $^{13}$C, $^{15}$N and $^2$H.

187. 77Se NMR spectroscopy of selenoproteins’ redox motifs

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Selenium, a vital element in the human body, is a cardinal contributor to cellular antioxidative defense and cancer prevention. Selenoproteins, which contain the reactive amino acid selenocysteine, participate in redox and electron transfer reactions. The 25 human selenoproteins are powerful enzymes that utilize the selenocysteine in conjunction with a nearby cysteine in their active site. These so-called redox motifs govern the protein redox potential and hence chemical reactivity. We measured the differences in the inherent flexibility of selenocysteine in different redox motifs: the cysteine-selenocysteine redox motif is present in thioredoxin reductase while the cysteine-X-X-selenocysteine redox motif (X stands for any amino acid) is found in cell signaling selenoproteins. $^{77}$selenocysteine was incorporated into proteins by manipulating E. coli selenium incorporation machinery. We have measured the relaxation properties of the selenium in the redox motif using solution-state selenium NMR. Our NMR data show that the selenocysteine in the oxidized cysteine-selenocysteine redox motif is much more rigid than that of the cysteine-X-X-selenocysteine redox motif. In contrast, the flexibility of the active site selenocysteine is greater in the reduced cysteine-selenocysteine than in the reduced cysteine-X-X-selenocysteine redox motif.

Chemical Education Poster Session II
Organizer: P. Deshong

188. A Proposed Method to Ascertained Racial Differences in Hair Structure Using Proteomics

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In Chris Rock’s 2009 documentary “Good Hair,” Rock explains some of the treatments used by African-American women to straighten their naturally “nappy” hair. Such treatments include the use of hair straightening chemicals known as hair relaxers, which are composed of sodium hydroxide in a pH range of 10-14. Said strong base breaks down the secondary, tertiary, and quaternary
interactions between the hair proteins, which thereby causes the hair to straighten. This form of hair relaxer is highly caustic, damages the scalp, and is painful to apply. As of now, the differences in the chemical or protein structure of “African” hair and straight hair are not known. I have proposed a method to determine such differences using proteomics. In the proposed method, different types of hair are separately dissolved in an aqueous solution comprising a chaotropic agent such as urea or lithium perchlorate, and a reducing agent such as 2-mercaptoethanol. High molecular weight fibrous protein is separated from low molecular weight matrix proteins via centrifugation. Protein samples are subsequently analyzed with gel electrophoresis and stained for total protein using a stain such as Coomassie Blue. See Dekio et al. J Dermatol. 1990 May;17(5):269-75.

Subsequent to this, protein-containing spots are cut from the gel, destained, extracted, digested with trypsin to form peptides from proteins, and the peptides analyzed on a standard electrospray mass spectrometer in positive ion mode coupled to a liquid chromatograph, as is done in standard proteomics experiments. Various algorithms exist to analyze proteomics data.

Such a project would be useful because a knowledge of the protein chemistry of African hair may lead to the creation of a new hair relaxer that is less toxic and less painful to apply. Also, such a project may promote interest in science among African-American students in America or in African countries.

189. 5-aminovaleric acid adsorption to montmorillonite surfaces: Theoretical calculations

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Novel organo-modified clays involving 5-aminovaleric acid have been considered for applications as diverse as bone biomaterials and improved chelating agents for heavy metals. In this work, surface complexes of 5-aminovaleric acid on montmorillonite were modeled with three levels of theory. Initially molecular mechanics with the MMFF potentials were used to energy minimize systems with 5-aminovaleric molecule intercalated in a montmorillonite interlayer space. The interlayer spacing was estimated by minimizing several initial configurations. A quantum mechanical calculation at the semi-empirical level with the PM3 approximation was then used to provide vibrational frequencies to compare to values in the literature. Density Functional Theory calculations with Gaussian 09 to determine more accurate vibrations will be carried out on a reduced portion of the clay.

190. Theoretical calculations of the adsorption of lysine on montmorillonite surfaces

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This study is to observe the interaction of lysine, an essential amino acid with the surface atoms of montmorillonite, a widely used clay in pharmacology (as a stabilizer of suspensions and emulsions), and a drug carrier in drug delivery systems (i.e. for controlled drug release, gene delivery, and for drugs targeting a specific tissue). According to the pH, Lysine’s molecular structure changes, gaining or losing hydrogen ions. This research focuses on the cationic and zwitterionic states of the amino acid in a pH range of 4.9 through 9.7. The molecular mechanics energy minimizations performed with the Spartan package on two different states of Lysine in aqueous solution provide preliminary vibrational frequencies to compare with experiment. Density Functional Theory calculations of the vibrational infra red and Raman spectra of lysine surface complexes based on small portions of the clay will be discussed.
191. **Heavy metals in golf balls and fishing lures by x-ray fluorescence (xrf) spectrophotometry**

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Heavy elements, i.e. heavy metals, are considered to be health and environmental hazards. There are strict restrictions on the limits of these elements in drinking water, food, dishware, etc. In spite of the above, heavy metals can be found in a surprising array of things that consumers use every day. Plastics, glass, ceramics, alloys are the materials from which the items such as keys, flash lights, golf balls, fishing lures, etc. are made. All these materials, hence the items, contain heavy metals.

We have used X-ray Fluorescence Spectroscopy to determine the amount of heavy metals in many household items. Our latest interest has centered on the heavy metals content in both the exterior and interior of various brands of new and used golf balls. We are interested to determine whether the amount of these metals in the golf balls decreases with time, i.e. whether any leaching of heavy metals into the environment can occur. In addition, we expose the golf balls to various possible environmental conditions simulated in our laboratory, such as acid rain and heat for example, to observe whether the rate of heavy metals leaching into the environment increases if the golf balls are exposed to these extreme conditions.

192. **Heavy metals in everyday items by x-ray fluorescence (xrf) spectrophotometry**

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Heavy elements, i.e. heavy metals, are considered to be health and environmental hazards. There are strict restrictions on the limits of these elements in drinking water, food, dishware, etc. In spite of the above, heavy metals can be found in a surprising array of things that consumers use every day. Plastics, glass, ceramics, alloys are the materials from which the items such as keys, flash lights, golf balls, etc. are made. All these materials, hence the items, contain heavy metals. We have used X-ray Fluorescence Spectroscopy to determine the amount of heavy metals in many household items.

193. **Glycolate alkylations with 2-(methyliodo)acrylates toward the synthesis of majorynolide & majorenolide**

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The natural products majorynolide and majorenolide exhibit cytotoxic activities in human tumor cells. However, a synthetic pathway to construct these molecules has yet to be disclosed. Our laboratory’s approach toward these natural products envisions the application of a novel asymmetric glycolate alkylation, using Evans’ oxazolidinone as the chiral auxiliary, with 2-methyliodoacrylic esters. Synthesis of the requisite ethyl-, isobutyl-, and t-butyl-2-(methyliodo)acrylates was accomplished applying a known three-step process. Primary results for the alkylation of (S)-p-methoxybenzylglycolyl-i-propyl-2-oxazolidinone demonstrate the viability of employing t-butyl-2-(methyliodo)acrylate as an electrophile, providing products in good yield with >95:5 diastereoselectivity. Alkylation with the ethyl derivative gave various products, most likely resulting from reaction at the alkene terminus as well as the ester carbonyl. Successful alkylations are proposed to occur via an SN₂’ pathway. This project is currently focused on hydrolysis of the robust ester, and future chiral auxiliary removal with
concomitant lactonization, olefin metathesis, and protecting group removal should provide facile ac-

194. Catalytic, solvent-free preparation of $N$-(2-(pyridin-2-yl)-ethyl) sulfonamides

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Over 90% of current drug candidates, agrochemicals, and other synthetic materials possess nitro-
gen-containing rings such as pyridine. Similarly, many known drugs contain sulfonamides, which
are renowned for their great capability as antibiotic agents. Although nitrogen-containing hetero-
cycles and sulfonamides both play a crucial role in the chemical and pharmaceutical industries,
very little research has investigated methodology which joins the two functional groups to form the
$N$-(2-(pyridin-2-yl)ethyl)sulfonamide backbone. Our laboratory has discovered an efficient method
to unite vinyl pyridines and sulfonamides via an aza-1,4-conjugate addition towards this goal. While
the poor electrophilic and nucleophilic properties of the reagents pose limitations for uniting the two
functional groups, the use of an inorganic base and ionic solvent facilitates this synthetic methodol-
gy. TBAI catalysis is proposed to be two-fold: (1) solvation of the reagents, and (2) $S_n\text{,}_2'$ activation
of the vinyl pyridine with iodide. Kinetic studies in the laboratory are ongoing to understand the role
and effect of each reagent on the reaction, as well as to discover an environmentally responsible and
cost efficient method to isolate the product free of undesired bis-alkylated or hydrolyzed byproducts.
195. Calculation of the degree of ionization of salts in aqueous solutions as a function of concentration using microscale freezing point determination measurements

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The degree of ionization of salts in aqueous solutions can be calculated using the Van’t Hoff factor in freezing-point depression calculation measurements. We have developed a microscale procedure that uses a LabPro interface and aqueous solutions that are as low as 40mg of the salt in 4 mL water. A systematic study of eight different salt solutions reveals that the degree of ionization decreases with increasing concentration of the salt. A correlation between different salt solutions that involve isoelectronic cations is made. The procedure is particularly significant for large freshman chemistry classes as it leads to minimal quantities of waste solutions. It is also significantly faster which allows multiple trials by the student in the same session.

196. A DSSP model of interaction between modified Poria cocos D-glucan and murine DECTIN1 receptor

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Poria cocos, a medicinal mushroom-fungus planted across the globe where herbal medicine is widely used, has been studied for the enhancement of immunity against tumors in mice. Among the various medicinal mushrooms, it has been known to carry anti-tumor bio-chemicals. Recently, it has been reported that modified D-Glucan from Poria cocos could interact with the murine DECTIN receptor resulting in enhanced potential to strengthen mice’s immunity. The addition of COOH and S=O bonds residues were reported to unfold the coiled D-Glucan to a linear structure. This project used the DSSP model to calculate the DECTIN receptor protein structure. Our result shows that the cysteine at site 119 in DECTIN1 is essential for the binding of the open-structured sulfated D-glucan, consistent with postulation of Chen at al, 2010. Extension to human receptor modeling is discussed. The DECTIN1 protein structures, mouse and human, were downloaded from the Protein Data Bank. The SWISS-MODEL including the DSSP calculation was used for the project. The SWISS-MODEL is a fully automated protein structure homology-modeling server, managed by the Swiss Institute of Bioinformatics.

197. Pathways to chemical technology education and careers: A student internship analyzing water quality.

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The City of New York’s Harbor Survey Program is a water quality monitoring program brought out by the Metropolitan Sewerage Commission in response to public complaints of degraded water quality affecting their life. It consists of 47 stations: 35 located throughout the harbor open waters and 12 located in smaller tributaries within the City. As an intern and a member of the scientists’ team I gathered water samples and analyzed them for the four indicators of water quality. These include a) fecal coliform (FC) bacteria, found in human and animal intestine b) secchi transparency, related to water clarity, c) dissolved oxygen (DO) level affecting aquatic life and d) chlorophyll ‘a’ that responds
to the environmental changes quickly. Our work dealt mostly with the last two indicators which will be presented in detail and the challenges associated with them will be described.

198. Reactivity of tris (trimethylsilyl) phosphite (TMSP): N-mustard-bisphosphonic acid of bicine

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Osteoclasts are bone cells that can be used in controlling bone formation by breaking up mineralized matrix from the organic bone. This type of bone resorption decreases in activity thanks to its antineoplastic characteristic defined by the alkylating agent, in this case, nitrogen-mustard groups. In this way, synthesizing N-mustard-bisphosphonic bicine will have the potential to become a bone chemotherapy agent and can be further purified for drug treatments in metabolic osteoclastic diseases. Reaction of the inexpensive Bicine with thionyl chloride will produce the bis N,N(2-chloroethyl) bicine acyl chloride. After identification by spectroscopic methods, the product will be reacted with 3x excess of TMSP followed by hydrolysis. The expected final product: the N-mustard-bisphosphonic bicine, which will combine the directive action of bisphosphonates to bone tissue and inhibit osteoclastic resorption with the antineoplastic activity of the mustard group. The target product, after studies of their biological activities, has the potential to become an improved drug for treatment of metabolic bone diseases.

199. Reactivity of tris (trimethylsilyl) phosphite (TMSP): Synthesis of the bisphosphonic acid of phenylalanine

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Studies have shown that bisphosphonates can focus on bone density and strength thanks to antiresorptive functions that program apoptosis in osteoclast cells. Nitrogen-containing bisphosphonates are known for their prevalent use in the treatment of osteoporosis, malignant hypercalcemia, bone metases as a result of prostate and/or breast cancer, and Paget’s disease. Through spectroscopical analysis, reacting the inexpensive phenylalanine with thionyl chloride allows us to monitor a common amino acid and study the interaction of the a-amino group in the reactivity of tris(trimethylsilyl) phosphite to yield the corresponding bisphosphonate derivative of phenylalanine. The nucleophilic reagent should create the P-C-P bond that is characteristic in inhibiting the natural metabolic process of biological phosphates. In this way, the synthesis of a bisphosphonic acid of phenylalanine will have the prospect to be used as a bone chemotherapy agent and can be further purified for treatments in prescriptive osteoclastic ailments.

200. Determination of the ionization constant of carboxylic acids using microscale freezing point determination measurements

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The standard freshman General Chemistry laboratory uses the freezing-point depression concept to determine the molar mass of a solute via the general equation

$$\Delta T_F = (K_p) \times (m) \times (i)$$

$$\Delta T_F = \text{freezing point depression (°C)},$$
K_f = the cryoscopic constant (°C/ molal) of the solvent

m = molality of solution (mol solute/kg solvent) and

i = van’t Hoff factor, characteristic of the solute degree of ionization

We have developed a microscale procedure that uses a LabPro interface and aqueous solutions that are as low as 0.1g of solute in 3 mL water to determine the ionization constant of five carboxylic acids (K_a = 10^{-1}-10^{-2}) using the van’t Hoff factor at different concentrations. The data are the first ones reported at the freezing point of water. Moreover our procedure uses much smaller quantities than the standard titration procedures which lead to potentially significant accumulations of waste chemicals.

201. Application of microbiology at the wastewater treatment plant of the New York City Environmental Protection (DEP)

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The Department of Environmental Protection (DEP) in New York City recycles wastewater after removing heavy metals, grease, fecal material and other microbiological pollutants. All city wastewater is collected at the Newtown Creek’s facility for treatment before being released. As an intern I was involved with the microbiology department using m-MFC broth with rosolic acid for the detection and enumeration of fecal coliforms by membrane filtration. The disinfection and digestion steps follow the preliminary, primary and secondary treatments. The digestion stimulates the growth of anaerobic bacteria, which decompose most organic substances in the sludge. As a result the sludge thickens after most of the material is converted into carbon dioxide and methane gas. The detailed procedure will be described with emphasis on the challenges encountered.

202. Recycling wastewater at New York City’s Division of Environmental Protection: An ATE grant summer internship

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Every day 4.8 billion gallons of water are used to just flush toilets. The Division of Environmental Protection (DEP) in New York City has implemented a conservation cycle to recycle quality water from wastewater. The Newtown Creek Plant recycles 310 million gallons of water daily and evaluates the data generated by the Microbiology Laboratory. Microbiologists use microscopic analysis of activated sludge through dark-field microscopy to observe the evolution of biosolids through endosymbiosis. As an intern I facilitated in the analysis of fecal coliform in citywide samples in order to determine the appropriateness of minimal chlorine use before discharge into the receiving waters. These receiving waters are channeled from wastewater in our homes to the laboratory for evaluation of the fecal count before chlorine treatment and subsequent discharge. The procedure, difficulties and ways to overcome these challenges will be presented.
203. The technology of biosolids as applied to wastewater at New York City’s Division of Environmental Protection

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The Newtown Creek Microbiology Laboratory specializes in the rising technology of biosolids that allows bacteria from old wastewater residue to feed off biosolids in new sludge which sink towards the bottom of egg-shaped digester tanks. Afterwards, a third of this accumulated sludge is used to fight younger, incoming sludge, a third is used to process methane gas that powers the plant while the leftover is converted into sludge cakes that are sent to rural farms as fertilizers. Since the biosolids in the activated sludge are constantly evolving, microbiologists must constantly examine sludge from different plants to ensure that old biosolids are ingesting newer colonies through activated sludge control and membrane filtration. As an intern I was a member of the team verifying effluent samples from the fourteen plants located throughout New York City before it is sent back to the Hudson-Croton Reservoir.

204. Determination of gallic acid in teas and other beverages using high pressure liquid chromatography

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Gallic acid, C₆H₄(OH)₃COOH, also known as 3,4,5-trihydroxybenzoic acid, is an organic acid, that is found in many varieties of nuts, herbs, tea leaves and other plants and has found many application sin the healthcare and pharmaceutical industry. A procedure has been developed that determines the amount of gallic acid present in various tea beverages, tea samples and other fruit and vegetable juices using High Pressure Liquid Chromatography (HPLC). The quantitative measurement uses a calibration curve produced with standard solutions of gallic acid. The preparation of the samples, treatment with sodium dihydrogen phosphate buffers as well as the identification and quantitative determination of the gallic acid content in these beverages will be described and comparisons will be drawn. Moreover similar studies on the same samples after left uncapped and exposed to air oxidation for a week were made, indicating a considerable decomposition of gallic acid with time. Preliminary studies in beer and wine brands appear to display similar trends.

205. Determination of copper content of the US penny by x-ray fluorescence and gravimetric method

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The gravimetric method is very important in quantitative analysis and has been used to investigate metal content in various samples. The method has been applied to determine the content of copper in US pennies as a part of the forensic science program. The gravimetric method was only applied to pennies of 1982 and older because the copper content of new pennies was too low to perform the method. The content of copper in US pennies varies according to the year of production. For example, pennies made from 1864 to 1982 (excluding 1943 and 1974) are homogeneous mixtures (brass) of 95% copper and 5% zinc. Pennies produced after 1982 contain only 2.5% copper plated on top of a 97.5% zinc core. The gravimetric method performed on 1960 to 1982 US pennies revealed that the
copper content of the pennies were 95±1%, which was agreeable to the result measured by the X-ray fluorescence.

206. Determination of copper content of the US penny by visible spectroscopy and x-ray fluorescence

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The content of copper in US pennies varies according to the year of production. For example, pennies made from 1864 to 1982 (excluding 1943 and 1974) are homogeneous mixtures (brass) of 95% copper and 5% zinc. Pennies produced after 1982 contain only 2.5% copper plated on top of a 97.5% zinc core. The copper content of the US pennies from 1960 to 2010 has been determined by two convenient methods of visible spectroscopy and X-ray fluorescence. The visible spectroscopic method gave consistent results for both types of pennies. The percent copper in the US penny in 1982 and older was found to be 95±1% while the US penny after 1982 was found to be 3.2±0.3%. X-ray fluorescence has proved to be very useful in determining the metal content of the pennies. Furthermore, it gave indirect evidence as to whether the penny was a homogeneous mixture (brass, 95±1% copper) or a heterogeneous mixture (copper-plated zinc, 24-46% copper).

207. Concentration dependence of refractive index measured by a laser pointer: Refractive index vs. concentration

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The refractive index of a compound can be used as an analytical technique for the purpose of identifying a specific liquid or solid compound. This technique, however, is rarely adapted to the undergraduate laboratory curriculum due to the dependence of an expensive refractometer in order to determine the refractive index. Moreover, the accessibility of the instrument would be limited to only a few students in the laboratory. Recently we have developed a simple, accurate and inexpensive system which entails the use of a laser pointer and chromatography column to accurately determine the refractive index of pure liquids, liquid-liquid mixtures, and temperature dependence. A good relationship was found between the refractive index and various types of concentration of acidic, basic, and ionic solutions. Furthermore, this system can be used to calculate the refractive index of a solid indirectly by extrapolating the line of the linear graph between the refractive index and percent mass of the solution to 100% (pure solid).

208. Temperature dependence of refractive index determined by a laser pointer: Simple and cost effective system

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The refractive index is a well-known analytical technique used to identify various compounds. This method, however, is rarely adapted to the undergraduate laboratory curriculum due to the fact that a proper and efficient setup had not been developed. Recently, we have developed a simple, accurate, and inexpensive system for determining the refractive index of various compounds using a laser pointer and chromatography column. The system has proved to be very accessible and accurate in measuring the refractive index of single and binary solvent systems. The laser pointer method has been further applied to determine the refractive index of organic liquids and water within the temperature range of −15°C to 125°C without the use of expensive equipment such as temperature...
control systems and refractometers. The results showed that there was a good trend between the temperature and the refractive index of the liquids.

209. **Using the Folin-Ciocalteau Method to measure the total amount of antioxidants in tea samples and other beverages**

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Many commercially available beverages contain variable quantities of antioxidants. In this project visible spectrophotometry is used to quantitatively measure the total concentration of antioxidants via the Folin Ciocalteau method in different brands of tea samples, juices and other beverages using Gallic acid as the standard. The Folin-Ciocalteau reagent, also known as Folin's phenol reagent or Folin-Denis reagent or Gallic Acid Equivalence method (GAE), is a mixture of phosphomolybdate and phosphotungstate ions. It is used in the colorimetric assay of phenolic and polyphenolic antioxidants in the wine industry. The Beer-Lambert law uses the intensity of the blue color formed when the reagent is in contact with the assay to measure the amount of the antioxidants present in the solution. However, this reagent does not only measure the total amount of phenols as it reacts with any reducing substance. Nevertheless the response to gallic acid has been shown to be equivalent to most other phenolics in wine on a mass basis and is therefore used to construct the calibration curve. This procedure was applied to both, tea and other fruit beverages, as well as tea bags and the effect of air decomposition of the antioxidants with time was measured. Preliminary results of the application of this method on beer samples will also be presented.

**Medicinal Chemistry Poster Session II**
Organizer: P. Deshong

210. **Potent and orally bioavailable, Benzazepine based Histamine-H₃ antagonists**

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The histamine H3 receptor is a GPCR protein that is primarily located in the CNS of many species, providing negative feedback regulation of histamine release. Antagonism of the receptor leads to an increase in CNS histamine levels and is shown to improve cognition and increase wakefulness in rodents. Our discovery team’s focus was to find a series of selective, orally-bioavailable H3 antagonists which enhance wakefulness and cognitive properties in rodents and eventually in humans. The synthesis and SAR surrounding a series of substituted pyridazinones and 4, 5-dihydropyridazinones linked to a benzazepine core will be discussed. Also the selectivity versus other histamine-receptor
family members (Histamine-$H_1$, $H_2$, and $H_4$), stability in liver microsomes, CYP inhibition, and pharmacokinetics in rats will be presented.

211. Synthesis and SAR analysis of a library of dihydroquinazolinone TSHR agonists

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The thyroid stimulating hormone (TSH) is an α/β heterodimeric glycoprotein hormone secreted from the anterior pituitary gland. It belongs to the glycoprotein hormone family and binds to the TSH receptor (TSHR). TSHR is mainly expressed in thyroid follicular cells, but is also found in the bone, brain, kidney, testis, endometrium, and immune system. The functions in many of these tissues are not fully understood and the development of a selective TSHR agonist could provide a valuable pharmacological tool for researchers interested in exploring this receptor. A selective agonist could also serve as an alternative to recombinant human TSH therapy. Previously, a library of 73,180 compounds was screened at NCGC and a novel dihydroquinazolin-4-one was identified as a selective TSHR agonist. We recently completed the synthesis and structure-activity relationship (SAR) analysis of a library of dihydroquinazolin-4-ones and identified a compound that was 5 fold more potent than our previous lead.

212. Towards the synthesis of novel CK1 inhibitors: An approach using a metal halogen exchange on 2-bormopyridines

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Vanessa Paradis*, Jenifer A. Bradley, Todd W. Butler, Kenneth Dirico, Paul Galatsis, Michael Green, Jianke Li, Wayne S. McDonald, Blossom Sneed, Chakrapani Subramanyam, Travis T. Wager

Casein kinase 1 (CK1) has been identified as a key regulatory factor in the control of circadian rhythms. Therefore, inhibitors of CK1 would be of therapeutic value in such indications as jet lag, shift work and psychiatric disorders. Chemical matter initially identified through a p38 program was used as a starting point for elaborating SAR towards CK1 inhibition. Building from the hinge binding pyridine moiety of the p38 inhibitor, metal halogen exchange methodology employing 2-bromopyridines was envisioned to provide access to novel substituted derivatives. This poster will discuss the development and optimization of this methodology in the preparation of cyclic amine substituted pyridines.

213. Flexible docking in tandem with linear discriminant analysis as a tool to generate hypotheses on the binding of agonists and blockers to G protein-coupled receptors

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Activation of G protein-coupled receptors (GPCRs) is a complex phenomenon that initiates with the binding of an agonist, propagates through a cascade of ligand-dependent conformational changes, and eventually results in the selective activation of a signaling pathway. Up until very recently, no
GPCR structures had been solved in complex with agonists. Thus, we devised a computational strategy intended to generate hypotheses on the conformational changes induced to the receptor by agonist binding, preliminary to the sequence of events that characterize activation of the receptor. Specifically, we targeted the crystal structure of the inverse agonist-bound β₂-adrenergic receptor with Induced Fit docking (IFD) experiments conducted in tandem with linear discriminant analysis (LDA). This analysis suggested that agonists induce subtle movements to the fifth transmembrane domain (TM5) of the receptor. In particular, a subtle displacement of Ser207 and a slight counterclockwise rotation of TM5 emerged as the features that most prominently distinguish agonist binding from blockers binding. Remarkably, the agonist-induced conformational changes subsequently revealed by Kobilka and coworkers through X-ray crystallography resulted in striking agreement with our hypotheses. Importantly, we also showed that the IFD/LDA procedure can be used as a computational means to distinguish agonists from blockers on the basis of the differential conformational changes induced to the receptor.

214. Design, synthesis, and evaluation of 2,3-Diphosphoglycerate analogs as stabilizer and affinity modulator of hemoglobin

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The usage of stroma free hemoglobin as a blood substitute is associated with two major problems. First, it suffers from short circulation time in the blood stream due mainly to its breakdown from a large tetrameric protein, α₁α₂β₁β₁, into two smaller dimeric units, α₁β₁ and α₂β₂, consequently facilitating its rapid renal elimination and afflicting considerable renal toxicity. Secondly an increase in the oxygen affinity of hemoglobin (Hb) limits the release of oxygen to the tissues. These drawbacks have been attributed to the loss of the natural allosteric effector of Hb, called 2, 3-diphosphoglycerate (DPG), upon isolation of pure stroma-free Hb from RBC. In this study, a series of analogues of 2, 3-DPG, specific to the β cleft, containing different replacement of the phosphate group were synthesized and characterized as a site-directed affinity reagent for cross-linking human and bovine hemoglobin. The compounds synthesized include phosphonates and difluoromethyl phosphonates analogues of 2,3-DPG. Various procedures have been used to make these DPG analogues. The first two of these diphosphoglycerate derivatives was tested for hemoglobin cross linking and oxygen binding affinity of the cross linked hemoglobin; however, neither oxygen affinity nor cooperativity was modified by the analogs. Other analogs which incorporate electrophile sites for possible covalent bond formation with the amine group on Hb, like ester groups, in the bridge are also synthesized and ready for the test. Human and bovine Hb are used for investigation of the cross linking and adjustment of oxygen affinity.

215. Protein polymer conjugates and curcumin conjugates for biomedical applications

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Bioconjugates with proteins is a multibillion dollar industry. The current technology of producing polymer bioconjugates is limited to a few monomers; the number of dyes/drugs that can be conjugated per protein without loss of bioactivity is limited. A general synthetic methodology to produce a range of living copolymer protein conjugates with an amplified loading of dyes/drug will be presented. Over 7500 research papers and 18 clinical trials support the potential of Curcumin (the active ingredient in the spice Turmeric) to treat a range of pathological conditions. Curcumin is poorly absorbed by the body thereby severely limiting its potential as a drug candidate. A comprehensive strategy
towards drug candidates with enhanced bioactivity based on Curcumin will also be presented.

216. **Hydroxy-pyrrolopyridine-trione Based HIV-1 Integrase Inhibitors**

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After more than two decades of intensive research, approximately 30 drugs have been approved by the FDA for the treatment of HIV/AIDS. Merck’s Isentress™ (MK-0518 or Raltegravir), the first FDA-approved HIV-1 integrase (IN) inhibitor, shares key structural features with other IN inhibitors. These features include a co-planar arrangement of heteroatoms that chelate magnesium ions and halogen-substituted aromatic functionality linked to the chelating portion of the molecule that interacts with a region formed between a viral DNA base and the protein in the IN•DNA complex. The emergence of Raltegravir-resistant IN mutants demonstrates a need to develop new IN inhibitors that can overcome this resistance. A co-crystal of Raltegravir bound to the Prototype Foamy virus (PFV) IN complexed with DNA [Hare, S. et. al. *Nature*, 2010, 464, 232-7] provides insights into the basis for the resistance caused by mutations in IN. We have previously reported 4,5-dihydroxy-1H-isooindole-1,3(2H)-diones as structurally simple IN inhibitors that exhibit good potency and strand transfer selectivity in vitro in the presence of Mg^{2+} cofactor. The co-crystal structure of one of these inhibitors bound to the PFV•DNA complex has recently been solved. This allows comparison to be made of the binding interactions of our synthetic inhibitors with Raltegravir. As reported herein, a series of hydroxy-pyrrolopyridine-trione-containing analogues were prepared by insertion of a nitrogen into the ring system of the original 4,5-dihydroxy-1H-isooindole-1,3(2H)-diones. This simultaneously combines structural features of our original inhibitors with Merck’s pyrimidinones IN inhibitors. The efficient synthesis of these compounds relies on the application of a “Pummerer cyclization deprotonation cycloaddition” cascade of imidosulfoxides as well as [3+2] cycloaddition of isomünchnones. Introducing a nitrogen substituent into the catechol ring to give the 2(1H)-pyridone moiety reduces collateral cytotoxicity and improves potency against IN mutants resistant to Raltegravir.
217. **Elucidation of the reaction between aryl-boronic acids and cis-diols**

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The reversible binding of diol-containing compounds to aryl-boronic acids, such as phenyl boronic acid (PBA), has been studied for over 50 years. Since the first report, boronic acids have been exploited extensively for their use as carbohydrate sensors. With the FDA approval of the first boron-containing pharmaceutical, Velcade™ (bortezomib), there has been great interest in the use of boronic acids for medicinal purposes. In this work, the reaction of PBA with the diol-containing, fluorescent dye Alizarin Red S (ARS) is probed, Figure 1. Both steady-state and pre-steady-state experiments have been used for the characterization of the reactions over a wide range of pH, from approximately 4 to 10. It will be shown that ARS reacts with both the boronic (neutral, trigonal) form as well as the boronate (anionic, tetrahedral) form of PBA, in contrast to the prevailing notion within the field.

218. **Synthesis and SAR studies of thieno[2,3-c]pyridine derivatives as novel small molecule inhibitors of the human apurinic/apyrimidinic endonuclease 1 (APE1)**

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DNA damage occurs via a variety of mechanisms including deamination, oxidation and alkylation. DNA base excision repair (BER) is one of the cellular mechanisms responsible for the repair of DNA damage by both endogenous (e.g. reactive oxygen species from metabolic byproducts) and exogenous sources (e.g. radiation (UV) and cancer chemotherapy/radiotherapy). BER is initiated by the action of DNA glycosylases which recognize and remove the damage base leaving behind an AP site which are subsequently cleaved by an AP endonuclease. Apurinic/apyrimidinic endonuclease (Ape1) accounts for ~95% of AP endonuclease activity in mammalian cells and thus is an essential enzyme in the BER pathway. Recent studies report up-regulation of Ape1 in numerous cancers including prostate, ovarian, cervical, brain and colon cancer. These findings have been further validated by several clinical and preclinical reports which suggest a link between high Ape1 levels and cancer resistance to chemo/radiotherapy. Thus, targeting Ape1 could improve the efficacy of current cancer treatment methods by inhibiting the ability to repair DNA damage caused by chemotherapy agents such as TMZ. Though a few small molecule inhibitors of Ape1 have been reported, most lack drug-like properties and thorough structure-activity relationship (SAR) studies have not been discussed. As such, we sought to identify novel small molecule inhibitors of Ape1 through a quantitative high throughput (qHTS) screen of the molecular libraries small molecule repository (MLSR). Through this effort we identified a thieno[2,3-c]pyridine derivative as an promising lead which exhibited _in vitro_ potency in the low µM range. Upon synthetic elaboration of this lead, we optimized potency and established an SAR profile around this molecule. Top compounds exhibit low µM potency against Ape1, activity...
in cell extract and potentiate the cytotoxic effects of MMS and TMZ against HeLa cells. Additionally, a significant increase in AP site accumulation occurred in MMS treated cells in the presence of these inhibitors suggesting an on-target effect. Selected compounds were characterized for their in vitro ADME and in vivo PK properties. Future studies will involve testing these compounds against a variety of cancer cell lines and ultimately mouse xenograft models.

219. Determining mechanisms of immune modulation by sorafenib in a HER2+ breast cancer model

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Sorafenib is a promiscuous small molecule tyrosine kinase inhibitor with anti-angiogenic activity. Initially designed to inhibit the RAF/MEK/ERK pathway, numerous studies have also reported inhibition of VEGFR-2/3, PDGFR-b, c-KIT, and Flt-3. Sorafenib has been FDA-approved for the treatment of hepatocellular and renal cell carcinomas, and is under active investigation for the treatment of other tumor types. Here, we assess the therapeutic potential of the multikinase inhibitor Sorafenib in a model of HER-2+ breast cancer. In vitro, Sorafenib inhibits the growth of the mouse HER-2-expressing breast tumor cell line NT-2.5, and induces apoptosis. Western blot analysis revealed that Sorafenib interferes with the ERK/MAPK signaling pathway, which is constitutively activated in the setting of HER-2 over-expression. Given the central role of the ERK/MAPK pathways in macrophage activation, we also examined the impact of Sorafenib on macrophage activation in vitro. Activated macrophages express different cytokine profiles that reflect distinct functional phenotypes. M1 (classically activated) macrophages, induced by proinflammatory mediators (lipopolysaccharide (LPS)), typically produce IL-12, and are associated with Th1-type responses. In contrast, M2 (alternatively activated/regulatory) macrophages, induced by anti-inflammatory mediators (LPS and PGE₂), typically produce IL-10, and are associated with Th2-type responses. Studies have shown that strong ERK activation skews macrophage cytokine secretion toward the regulatory, IL-10-secreting phenotype. We therefore sought to determine the impact of Sorafenib on the functional phenotype of macrophages. Sorafenib treatment of bone marrow-derived macrophages activated with LPS and PGE₂ skewed cytokine secretion from a predominance of IL-10 to a predominance of IL-12. Western blot analysis demonstrated that Sorafenib affected activation of STAT3, with a decrease in IL-10. Further, interrogation of the p38MAPK signaling pathway revealed that Sorafenib treatment inhibited p38 activation and subsequent activation of the downstream target MSK1. p38αMAPK, via MSKs, plays a key role in dampening macrophage inflammatory responses. These data show that inhibition of p38/MSK plays an integral role in the modulation of macrophage cytokine production in vitro. Numerous reports have shown that tumor-associated macrophages (TAMs) are immunosuppressive and tumor-promoting. Therefore, Sorafenib may have the potential to alter the functional phenotype of tumor-associated macrophages (TAMs) from a regulatory pro-tumor macrophage to a classically-activated anti-tumor macrophage. In the in vivo setting, we found that Sorafenib drives marked regression of HER-2-expressing tumors in non-tolerant FVB/N mice. In contrast, Sorafenib has minimal impact on tumor growth in tolerant neu-N mice, despite a substantial pruning of the tumor-associated vasculature as assessed by immunohistochemistry. Future studies aim to examine the effect of Sorafenib on TAMs in this model of HER-2+ breast cancer, and to explore the effect of Sorafenib-induced immune regulation on the breast tumor microenvironment.

220. Halogenated enaminones as potential anticonvulsant agents

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Background: Enaminones are compounds consisting of amino group linked to keto group through a carbon-carbon double bond. Halogenated enaminones have halogen atoms such as bromo, chloro,
fluoro, and iodo substituting for one or more protons in the enaminone molecule. Certain enaminones are known to have analgesic, anticonvulsant and anti-inflammatory activities. Our objective was to synthesize halogenated enaminones, and evaluate them for anticonvulsant effects in vivo and in vitro.

**Methods:** Beta-diketo compounds were prepared by three different synthetic routes, and condensed with appropriate halogenated amino compounds to yield the expected enaminones (1-30). Enaminones 1-18 were evaluated in vivo using standardized electrically-induced, and chemically-induced seizure models, and the rotorod test for neurotoxicity in mice and rats. Enaminones 19-20 were evaluated in vivo and in vitro, while enaminones 21-30 were evaluated in-vitro only. The anticonvulsant profiles of the most potent enaminones were compared to those of currently available anticonvulsants.

**Results:** In the in vivo evaluations, eight of the halogenated enaminones were class 1 anticonvulsants (active at 100 mg/kg dose), while three of the compounds were class 2 anticonvulsants (active below 300mg/kg dose) in the Antiepileptic Drug Development (ADD) program. For the enaminones selected for in vitro evaluation, four of them produced significant reduction of neuronal population spike in the rat brain. The halogenated enaminones were devoid of neurotoxicity in the rotorod test, when compared to phenytoin and carbamazepine.

**Conclusions:** The halogenated enaminones carrying mono-, di- or tri-substituted phenyl groups afforded potent anticonvulsant agents in the in vivo and in vitro evaluations. The halogenated enaminones 1-2 and 19-22 afforded lead compounds in the development of potent anticonvulsant agents with minimal toxicity.

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221. **Peptide-capped Gold Nanoparticles: Design, Characterization, and Their Application in Drug Delivery**

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Preparation and evaluation of gold nanoparticles (AuNPs) have become subjects of considerable interest in biomedical sciences because of their broad applications in biosensing, imaging, drug delivery, and cancer therapy. AuNPs are usually synthesized in the presence of inorganic reducing agents under harsh reaction conditions. Synthesis of AuNPs using inorganic chemical reagents is not an appropriate method for biomedical applications due to the toxicity of traces of remained reducing agents. L-Cyclic peptides can form diverse structures because of different physicochemical properties of the natural L-amino acid building blocks. L-Cyclic peptides are biocompatible and usually more stable than the corresponding linear peptides. An optimal balance of positive charge and hydrophobicity is required for electrostatic interactions with the cell membrane for deep penetration of peptides into the lipid bilayer. The application of cell penetrating cyclic peptides as reducing and capping agents of metal nanoparticles remains unexplored. Herein we report the synthesis and evaluation of a number of amphotipathic L-cyclic peptides containing hydrophobic and charged amino acids in generating and capping AuNPs. Among all the synthesized cyclic peptides, [WR]ₙ class where n = 1-3, showed higher efficiency in the synthesis and in-situ capping of AuNPs under mild conditions. TEM demonstrated that [WR]₄-AuNPs were in the size range of 10-100 nm. UV-Vis spectroscopy exhibited the formation of [WR]₄-AuNPs at 1 mM. Peptide-capped gold nanoparticles were determined to be not toxic at the concentration of 100 μM and were able to inhibit Src kinase with an IC₅₀ value of 2.8 μM. Furthermore, [WR]₄-AuNPs exhibited cell penetrating and molecular transporter properties of fluorescence-labeled lamivudine across cell membrane in SK-OV-3 and CCRF cells. In summary,
[WR] can be used to generate stable biocompatible gold nanoparticles with potential application for simultaneous cellular delivery of capped AuNPs and therapeutic agents.

222. Presence in human CYP1A2 gene of -163C>A SNP insufficient for predicting perceived caffeine sensitivity

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Caffeine is metabolized in the liver, primarily by the enzyme cytochrome P450 coded by the CYP1A2 gene. There are multiple alleles of the CYP1A2 gene which vary in the regulated expression of the enzyme, leading to interindividual differences in caffeine elimination rates. Recent research, widely covered in the popular media, linked specific CYP1A2 gene variants with increased caffeine consumption. The present study is a close companion, testing for a potential genetic basis to perceived individual reactions to caffeine. Two CYP1A2 alleles identified in the literature and used in caffeine metabolism phenotyping by personal genomics services, CYP1A2 *1C (SNP -3860 G>A), a slow metabolizer, and CYP1A2 *1F (SNP -163 C>A), a fast metabolizer, were tested to determine whether they are predictive of self-reported caffeine sensitivity or resistance, respectively.

Cheek cell DNA collected from volunteers who filled out surveys on caffeine intake and perceived sensitivity was subjected to polymerase chain reaction-restriction fragment length polymorphism assays (PCR-RFLP) to determine CYP1A2 genotypes for the defining single nucleotide polymorphisms (SNPs) of the *1F and *1C alleles. A separate DNA fragment encompassing the first exon of the coding region and the -163 SNP was then sequenced in hypersensitive individuals to determine if any other SNPs were present that might reduce enzyme activity. Individuals thus genotyped were then compared to their self-reported caffeine sensitivity.

Of about 20 DNA samples, only five individuals had the two SNPs of interest. No additional SNPs were found in the coding region. Four individuals had the SNP associated with the CYP1A2 *1F allele and only one with the *1C. When the genotyped individuals were then matched to their caffeine sensitivity surveys, the four *1F (one heterozygous) individuals were all self-reported hypersensitive, similar to the *1C allele individual. These results show the presence of fast or slow metabolism SNPs alone are not the key factor determining whether individuals are sensitive or resistant to caffeine.

223. Expression and Purification of Mycobacterium tuberculosis Sigma Factor (SigA) for in vitro transcription assays

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Mycobacterium tuberculosis (MTB) is a pathogenic bacteria responsible for 2 million annual deaths and infections of nearly a third of the global population. The MTB transcription complex is a viable target for current and prospective antibiotics. As part of a larger project designed at optimizing an in vitro transcription assay featuring MTB RNA polymerase (RNAP)-sigA holoenzyme, the expression and purification of native sigA protein was a necessary step. SigA is the primary/"housekeeping" sigma factor for MTB. It is responsible for promoter recognition of the MTB housekeeping genes and is vital to transcription initiation. Previous work within the Garica lab noted mis-folding and aggregation of sigA when purified as expressed from a pET plasmid in transformed E. coli. To improve the solubility and recovery of the protein, the sigA gene was subcloned into the pAvitag plasmid system and expressed in E. coli. The recombinant sigA protein expressed features a six residue histidine tag and an AVITAG for use in nickel affinity chromatography and to improve solubility, respectively. The cell lysis and protein purification procedures required optimization in order to yield native sigA. Due to an unusually slow migration on SDS-PAGE, the identity of this protein had to be confirmed via mass spectrometry. Work is on-going confirming the interaction of RNAP and sigA via preliminary
transcription assays. The ultimate goal for the overall project is the design of an in vitro transcription assay amenable to high throughput screen (HTS) for novel MTB antibiotics. In addition to HTS for novel leads, this assay will also be used to characterize designed inhibitors in collaboration with Prof. Hollis Showalter (Medicinal Chemistry Department, University of Michigan).

224. Discovery of Novel Macrolide Antibiotics

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The rapid emergence of antibiotic-resistant bacteria represents a serious health threat that shows no signs of abatement. A sharp decline in the number of pharmaceutical companies with active antimicrobial research programs underscores the need for new sources of antibiotics. As a part of a rational structure-based drug design program, we apply the paradigm of natural product structural simplification (i.e., desmethylation) to the 3rd-generation macrolide antibiotic telithromycin (2) & cethromycin (3), which are FDA-approved semisynthetic analogues of erythromycin (1) with (2) being in clinical use since 2004. The rationale behind desmethylation comes from crystallographic studies of 1 and 2 bound to ribosomal subunits, which corroborate biochemical mechanisms of antibiotic resistance (e.g., ribosomal modification and mutation). We have recently accomplished the de novo synthesis of 4,8-didesmethyl telithromycin (4) & 4,8,10-tridesmethyl cethromycin (5), which were found to be biologically active against both wild type and mutant bacterial strains and comparable to 2 & 3 in potency.

225. Receptor specific vasopressin antagonists

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Antagonists of arginine vasopressin, a 9 amino acid cyclic peptide with 3 known receptor subtypes (V₁a, V₁b, and V₂), are clinically used for treatment of hypertension, hyponatremia with or without concomitant congestive heart failure (CHF), and are in development as new therapeutics for dysmenorrhea and stress-related mood disorders. Azevan Pharmaceuticals Inc. has developed a unique
platform molecule with specificity for the $V_{1a}$ receptor as a novel class for CNS disorders including
major depression, intermittent explosive disorder, impulse control/anger disorders, and post-trau-
matic stress disorder (PTSD). Most members of the compound library possess four chiral centers and
research has shown that the general pharmacophore can be viewed as composed of four zones (A
through D) of potential variation (see figure below). The synthetic pathway to the API requires the
use of asymmetrically-induced loci and incorporation of chiral building blocks under non-racemizing
conditions. Two lead compounds have successfully completed Phase 1 trials and Phase 2A Proof-
of-Concept studies are planned. The synthetic routes to the class and the structure-activity for $V_{1a}$
antagonism will be presented.

226. Broad Spectrum Anticancer Activity of 5:7:5-Fused Diimidazodiazepine Analogues

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Nucleoside and nucleotide analogues containing the tricyclic 5:7:5-fused diimidazodiazepine ring
system are expected to be useful probes in mechanistic understanding of formation and repair of
such cross-links. We have also discovered that these compounds alone possess potent \textit{in vitro} ant-
nineoplastic activity in cancers of lung, breast, ovary and prostate. We, herein, report our efforts in
this series related to enhancement of activity and solubility.

Organic Chemistry Poster Session II
Organizer: P. Deshong

227. Stereodynamic probe providing a chiroptical response to substrate controlled induction of an axially chiral arylacetylene framework

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A stereodynamic probe containing a central 1,4-di(phenylethynyl)benzene rod and two 2-formyl-
phenylethynyl branches has been prepared through a series of Sonogashira cross-coupling reactions.
This CD silent probe carries two terminal aldehyde groups and is locked into a macrocyclic structure
upon condensation with amines. The central chirality of the substrate dictates the axial chirality of the diimine-arylacetylene framework, thus providing a strong chiroptical response. The chiral amplification results in intense Cotton effects that can be used for in situ ICD analysis of the absolute configuration and ee of a wide range of amines.

228. Synthesis of Chiral Tertiary Trifluoromethyl Alcohols by Asymmetric Nitroaldol Reaction with a Cu(II)-Bisoxazolidine Catalyst

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Bisoxazolidine (+)-1 is an effective ligand in the Cu(II) catalyzed Henry reaction with trifluoromethyl ketones. A wide range of tertiary alcohols derived from aliphatic and aromatic substrates were obtained in high yield and enantiomeric excess. This procedure has several merits including simplicity of operation, relatively short reaction times and wide functional group tolerance. In particular, the unprecedented stereocontrol observed for the reaction with nitroethane extends the scope of this reaction.
229. Enantioselective Friedel-Crafts reaction with indoles and ethyl trifluoropyruvate

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The asymmetric Friedel-Crafts reaction with indoles and ethyl trifluoropyruvate using a bisoxazolidine-derived Cu(I) complex as catalyst will be discussed. Effects of solvent, metal salt, temperature, catalyst loading etc. on yields and asymmetric induction were studied. Employing 5 mol% of copper(I) trifluoromethanesulfonate toluene complex and 6 mol% of an indanol-derived bisoxazolidine ligand in diethyl ether at -60 °C to -98 °C, a series of ethyl 2-(3'-indolyl)-3,3,3-trifluoro-2-hydroxypropanoates was obtained in up to 99% yield and 94% ee.

230. A Nickel(0)-Catalyzed Formal Aza-Nazarov Cyclization for Isoindolinone Synthesis

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Isoindolinones comprise the core structure of a number of biologically active compounds. We have discovered that this heterocycle can be easily prepared from readily accessible N-benzoyl aminals using nickel-based catalysts. Reaction optimization and substrate scope is presented, as well as mechanistic studies for this formal aza-Nazarov cyclization.
231. Cationic chiral dirhodium carboxamidates as Lewis acid catalysts

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Cationic chiral dirhodium(II,III) carboxamidates, obtained from oxidation of dirhodium(II,II) carboxamidate precursors with nitrosonium salts, have been verified to be efficient promoters in asymmetric Lewis acid catalyzed reactions. High regiocontrol and stereocontrol have been achieved with cationic chiral dirhodium(II,III) carboxamidate having \((R)\)-menthyl \((S)\)-2-oxopyrrolidine-5-carboxylate ligands in 1,3-dipolar cycloaddition reactions of nitrones with \(\alpha,\beta\)-unsaturated aldehydes, and for higher rates and selectivities in hetero-Diels-Alder and carbonyl-ene reactions with the diastereomeric catalyst having \((S)\)-menthyl \((S)\)-2-oxopyrrolidine-5-carboxylate ligands. Dramatic solvent influences on reaction rates and selectivities characterize the behavior of cationic chiral dirhodium(II,III) carboxamidates, with toluene being optimal for reactivity and selectivity. The reaction scope and solvent effect will be discussed.

232. Synthesis and applications of functionalized diazoacetoacetates

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Vinyl diazoacetate \(2\) can be conveniently prepared from acetodiazooacetate \(1\). Addition of silyl enol ether \(2\) and ortho formates \(3\) catalyzed by zinc triflate gives diazoacetoacetates \(4\) with acetal functionality. Only 1 mol\% Lewis acid is needed to catalyze this transformation and good yield is obtained. Compound \(4\) undergoes dinitrogen extrusion catalyzed by dirhodium catalyst to produce substituted cyclobutanone \(5\) and compound \(5\) is a useful synthon that upon ring opening leads to zwitterion \(6\) which readily undergoes cycloaddition and other transformations to give dihyrdo-Y-pyrone \(7\) and pyrazole \(8\) as products.
233. Amine heterocycle synthesis via rhodium(I)-catalyzed intramolecular hydroacylation

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Research in our laboratory is directed at exploiting the mild and selective rhodium-catalyzed hydroacylation as a strategy for the rapid construction of medium ring heterocycles. Alkenyl- and alkynyl-substituted 2-aminobenzaldehydes, upon treatment with Wilkinson’s catalyst, yield nitrogen heterocycles. Interestingly, the success of the reaction is dependent upon the identity of the non-reacting amine substituent, R. Seven- and eight-membered rings are accessible by this chemistry and the reaction tolerates substitution on the alkene or alkyne. The use of cationic rhodium catalysts, such as [Rh(dppe)]BF$_4$, instead of Wilkinson’s catalyst, increases the variety of heterocyclic amines that can be prepared using this chemistry.

234. Blue bottle reaction: Revised

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Oxidation of glucose by O$_2$ in an alkaline solution in the presence of methylene-blue, popularly known as the “blue bottle reaction”, has been reported to produce gluconate and water.
While investigating the bio-mimetic nature of this reaction, we found that the product of reduction of O₂ is in fact hydrogen peroxide (H₂O₂) instead of water as has been reported.

The reaction can now be studied using ABTS and horseradish peroxidase assay for H₂O₂. Ascorbic acid, an antioxidant of biological importance, also produces H₂O₂ under similar conditions. The glucose reaction products are identical to the products of biological enzymatic oxidation of glucose, suggesting the possibility of a similar mechanism for these reactions. A revised mechanism is proposed for the blue-bottle reaction.

235. Versatility of calixarene reactions with 1,3-dibromopropane

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Calixarenes are macrocyclic molecules and are useful building blocks for host molecules with different properties. They possess the ability to hold metal ions, as well as molecules, in their interior. Construction of larger and deeper molecular containers is also possible by using calixarenes. The goal of this research is to synthesize self assembling capsules and possible complexes based on two cone calix[4]arenes. In an effort of synthesizing this molecular capsule, a strategy was sought that would enable bridging the phenolic oxygens and rigidifying the cone calixarene. Among the various routes attempted to rigidify calixarenes, reactions of calix[4]arene with 1,3-dibromopropane was one of them.

Treatment of calix[4]arene with 1,3-dibromopropane in a 1:10 ratio, using K₂CO₃ in CH₃CN, gave 1,3-bis(3-bromopropoxy)calixarene as the major product together with small amounts of two new calixarenes. One was identified as a tetrakis(3-bromopropoxy)calixarene with a partial cone conformation. The structure was assigned by NMR (¹H, ¹³C, DEPT, COSY, HMQC, HETCOR), MALDI-TOF MS, and by X-ray diffraction. The other was identified as a 1,3-bis(3-bromopropoxy)calixarene having one bridge, with a flattened cone conformation. The structure was assigned by NMR (¹H and ¹³C), MALDI-TOF MS, and by X-ray diffraction. A similar experiment in which the ratio of calix[4]arene to 1,3-dibromopropane was 1:1 gave a biscalixarene as the major product, together with the 1,3-bis(3-bromopropoxy)calixarene. However, the reactions of calix[4]arene with 1,3-dibromopropane, using NaH in DMF, surprisingly produced the allylated compound, tetrakis(allyloxy)calixarene. Treatment of the tetrakis(allyloxy)calixarene with Grubbs first generation catalyst gave a mixture of products from which a new biscalixarene was isolated. The structure was assigned by NMR (¹H, COSY, HMQC), MALDI-TOF MS, and by X-ray diffraction.
In an attempt to rigidify cone calixarenes new compounds have been synthesized and some of these new compounds have potential applications as complexing agents. Studies in the use of other reagents to prepare bridged calixarenes are underway.

236. Synthesis and study of capped and tetrachelate/dichelate porphyrin chromophores on metal oxide semiconductor surfaces

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Tetraphenylporphyrin chromophores are studied extensively as possible sensitizers in dye sensitized solar cells. The study of interfacial electron transfer processes at dye/semiconductor interfaces is an active area of research due to possible applications in solar cells and catalytic devices. Many fundamental processes occurring at the dye/metal oxide interface are still not known and need careful consideration. The two aspects we will discuss here are a) the design and synthesis of tetrachelate/dichelate porphyrins towards ”isolation” of the chromophore on metal oxide semiconductor nanoparticle surfaces. This approach may limit the porphyrin-porphyrin stacking as well as undesired contacts with the semiconductor by constraining anchor group’s orientation. A novel synthetic strategy and characterization will be discussed. b) the electronic structure and energy level alignment of zinc and free-base tetracarboxyphenylporphyrins adsorbed on ZnO (11-20) single crystal surfaces, using direct and inverse photoemission spectroscopies and UV-visible absorption spectroscopy.

237. Functionalized catanionic surfactant vesicles for drug delivery and vaccine applications

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Catanionic surfactant vesicles are currently being studied as alternatives to conventional phospholipid liposomes for drug delivery, vaccine development, and in vitro diagnostic testing. Catanionic surfactants vesicles are attractive due to their inexpensive components, ease of preparation, and stability. These vesicles form spontaneously in aqueous solutions from the surfactants sodiumdodecylbenzene sulfonate (SDBS) and cetyltrimethylammonium tosylate (CTAT) and can be further modified by surface-functionalization using nonionic surfactants. We are currently studying the incorporation of various water insoluble drug molecules (i.e. lutein, maytansine, and taxol) into surfactant vesicles for use as potential in vivo drug carriers. The ability to functionalize the surface of these vesicular systems allows for targeting toward specific tissues, making them promising candidates for targeted drug delivery applications. Vesicles are also being developed into vaccines against gram-negative bacteria (e.g. Neisseria gonororrhoeae). Due to the poor immune response of other carbohydrate-based vaccines, peptide epitopes known to elicit an immune response were incorporated into vesicles along with the respective bacterial lipopolysaccharide. As a result, surfactant vesicle-based vaccines triggered a high IgG response in mice.
238. Cyclopropyl Aziridines: Solvolytic Reactions of the Tosyl Aziridine of (+)-2-Carene

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The tosyl aziridine 2 of (+)-2-carene 1 has been prepared, and solvolytic reactions of it with weak protic acids studied.

239. Novel ring expansion of a vinyl cyclopropane to a vinyl azetidine via a cyclopropyl bromonium ion

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Vinyl cyclopropane (+)-2-carene 1 underwent a novel ring-expansion of the cyclopropane when reacted with chloramine-T and catalytic phenyltrimethylammonium bromide. Novel azetidine 2 was obtained. The reaction proceeds via a cyclopropyl bromonium ion which undergoes a double ring-opening, followed by cyclization to the azetidine.

240. Membrane anion transport of alkylamido Ceramide analogues

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Ceramide is a membrane active Sphingolipid that plays important roles in regulation of multiple cellular processes, including apoptosis. Recently it has been shown that ceramide can be used as an ion carrier as well as channel forming receptor for binding and transportation of anions. Inspired by ion transport performance of this compound, a library of synthetic analogues of Ceramide is prepared that interestingly present ion transport properties with different transport kinetics. In this comprehensive study, different factors which can influence the rate of the transport have been studied.
241. Amino acid derivatives as ion transporters
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Ion transporters facilitate the transport of charged ions across the cellular membranes. Misregulation of ions can lead to diseases such as Cystic fibrosis and Bartter syndrome. Natural products such as ceramides, prodigiosin and valinomycin can act as ionophores. In particular, ion channels in nature make use of amino acid residues to selectively bind and transport ions. In this study, derivatives of natural and unnatural amino acids such as serine are being utilized for their ion transport properties.

242. Electrochemical Studies of Ketone : Lewis Acid Interactions
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The interaction of ketones such as 9-fluorenone and benzophenone with various Lewis acids has been investigated in ionic liquids using voltammetric techniques. Complexation of the ketone carbonyl group with a Lewis acid results in a positive shift of the ketone reduction potential, with an accompanying decrease in the voltammetric features for the uncomplexed ketone. Lewis acids such as Hf4+ and Sc3+, as well as some lanthanides, have been recently studied in this work. The ionic liquids 1-butyl-1-methylpyrrolidinium triflate and 1-ethyl-3-methylimidazolium tetrafluoroborate have been used. The former ionic liquid allows investigations to very negative potentials, providing useful information on ketones which are not easily reduced.

243. Improved process for the preparation of PhINTs
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[N-(p-Toluenesulfonyl)iminol-phenyliodinane, commonly abbreviated PhINTs, is an important reagent used as a nitrene source in reactions such as alkene aminations and aziridinations. However, its use is greatly hindered by inherent problems in the known preparations, which cause poor yields and potential safety concerns. Here a new process is presented that obviates these problems.

244. New HNO precursors based on bis-acylated hydroxylamines, N-acyloxsulfonamides, and N-hydroxy-N-acylsulfonamides
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The biochemistry of the nitroxyl system (NO/HNO), the one-electron reduced congener of nitric oxide (NO), has recently received significant attention, especially as a potential alternative to current treat-
ments of cardiac failure. Compared with NO, however, much less is known about the fundamental solution chemistry of this deceptively complicated system. Due to its inherent reactivity, HNO must be generated in situ, but only a very limited number of appropriate precursors currently exist. Adding to the difficulty of studying HNO chemistry is that a viable method for its direct detection in solution or biologically relevant preparations is not currently available. This presentation will focus on the development of new HNO precursors based on bis-acylated hydroxylamines, N-acyloxy sulfonamides, and N-hydroxy-N-acylsulfonamides. Synthesis and HNO generation mechanisms will be discussed.

245. Synthesis of quaternary centers mediated by a hypervalent iodine reagent and its application to total synthesis

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An innovative and rapid access to highly functionalized compounds, containing quaternary centers, is mediated by the use of a hypervalent iodine reagent. These quaternary centers, which can be linked to two, three or four sp2 carbons, would be difficult to obtain using conventional chemistry. This new methodology, which could be themed “aromatic umpolung”, allows a rapid access to elaborated cores, often found in a plethora of biologically active natural compounds. The synthesis of these natural compounds is therefore rendered more effective by the lesser amount of steps necessary to achieve such cores. Hypervalent iodine reagents also represent a valuable alternative to the use of toxic heavy metals, often used in chemical transformations, and are therefore in agreement with the “green chemistry” concept. The application of this novel methodology to the total synthesis of natural compounds is demonstrated by the oxidative versions of the Hosomi-Sakurai and Friedel and Crafts reactions, representing the key step in the synthesis of aspidospermidine and mesembrine. The potential of the oxidative version of Wagner-Merwein type transposition for synthetic purposes will also be discussed.

246. Stereoselective synthesis of substituted cis-hydrindanes

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The cis-hydrindane motif is found in many natural products with biological activity. Much effort has been made by chemists to afford diverse cis-hydrindanes. Many synthesized hydrindane compounds served either as precursors in total syntheses of natural products, or as promising scaffolds for drug development. Starting from readily available materials, we were able to approach a new class of substituted cis-hydrindane with high diastereoselectivity. The pendent side-chains on these cis-hydrindanes are highly functionalizable, and so could be easily modified to further expand the structural diversity of these bicyclic scaffolds.
**247. Self-assembly of small organic molecules in aqueous solutions**

**Deepa Subramanian**

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Motivated by controversies in the literature regarding the microscopic and mesoscopic inhomogeneities in some aqueous solutions we have performed static and dynamic light-scattering experiments in aqueous solutions of tertiary butyl alcohol. In addition to the molecular scale concentration fluctuations, we have found the presence of reproducible mesoscopic inhomogeneities, which become especially pronounced below room temperature. We find that the observed inhomogeneities are near-spherical Brownian particles, about a hundred nanometer in size, triggered by minute traces of specific impurities (in particular, propylene oxide) present in the solution. We speculate that these aggregates are long-lived, clathrate-like precursors formed due to the coupling between the intrinsic fluctuating nature of tertiary butyl alcohol aqueous solution and the clathrate-promoting ability of propylene oxide.

**249. Bisphosphonamidate clodronate prodrug exhibits potent anticancer activity in A549 NSCLC cells**

**Marie R Webster**

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Bisphosphonates are used clinically to treat disorders of calcium metabolism, hypercalcemia and osteoporosis, and malignant bone disease. Although these agents show anticancer effects, their use as anticancer agents for the treatment of extraskeletal disease is limited as a result of poor cellular uptake. The non-nitrogen-containing clodronate exhibits minimal activity against cancer cell lines, including both SCLC and NSCLC. We have designed and synthesized a bisphosphonamidate prodrug of clodronate requiring minimal bioactivation events to unmask multiple negative charges intracellularly. We demonstrate efficient bisphosphonamidate activation and significant enhancement in anticancer activity of two bisphosphonamidate prodrugs *in vitro* compared to the parent bisphosphonate.

**250. 1-Deoxy-D-xylulose 5-phosphate synthase: A new twist in thiamine diphosphate-dependent enzymology**

**Leighanne A Brammer**

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Emerging resistance of human pathogens to anti-infective agents make it necessary to develop new agents to treat infection. The methylerthritol phosphate (MEP) pathway has been identified as an anti-infective target, as this essential isoprenoid biosynthetic pathway is widespread in human
pathogens, but absent in humans. The first enzyme of the pathway, 1-deoxy-D-xylulose 5-phosphate (DXP) synthase, catalyzes the formation of DXP via condensation of D-glyceraldehyde 3-phosphate (D-GAP) and pyruvate in a thiamine diphosphate (ThDP)-dependent manner. Structural analysis has revealed a unique domain arrangement suggesting opportunities for the selective targeting of DXP synthase; however, reports on the mechanism of catalysis are conflicting. We are pursuing mechanistic studies of DXP synthase toward a long-term goal to develop selective inhibitors of early-stage isoprenoid biosynthesis. Here, we present the results of tryptophan fluorescence binding and kinetic analyses of DXP synthase, and propose a new model for substrate binding and mechanism. Our results are consistent with a random sequential mechanism, which is unprecedented in this enzyme class.

251. Reversibility of HNO-induced sulfinamide formation

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Cysteine residues are susceptible to several post-translational modifications under oxidative conditions. HNO, a potential heart failure therapeutic, is known to be very thiophilic. The reaction of HNO with thiols results in the formation of disulfide or sulfinamide, depending on the concentration of thiol. Traditionally, sulfinamide modification is considered to be irreversible in peptides and proteins. We have investigated the reversibility of HNO-induced sulfinamide formation in small organic molecules, peptides and proteins under physiological conditions. Proteins are known to undergo succinimide-mediated Asn deamidation at physiological pH and temperature. We hypothesized that the reversibility of sulfinamide modification might be facilitated in peptides via a similar mechanism. It is shown that, in the presence of reducing agents, sulfinamide formation is reversible. Moreover, the sulfinamide reduction is increased by at least a factor of three in the peptide structure vs. in small organic molecules. Although peptide sulfinamides are prone to hydrolysis, it is slower than the reaction with thiols. Activity studies with a cysteine protease, papain, demonstrates the feasibility of sulfinamide reduction in a protein environment. We conclude that there is a significant contribution from a low energy, cyclic intermediate (analogous to that in Asn deamidation) in the reversibility of peptide sulfinamides.

252. Inhibition of Francisella novicida growth in Conditioned Media: Biosignaling mechanism

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Francisella tularensis is a causative agent of the disease Tularemia. We hypothesized that F. tularensis performs quorum sensing using a two-component histidine kinase sensor system (QseC/QseB) and its signaling hormone-like molecule autoinducer (AI). The accumulation of the signaling molecule
and its interaction with transmembrane QseC protein initiates the cascade of reactions where the response regulator QseB and other intracellular proteins undergo autophosphorylation, and result in the expression of bacterial genes.

Prior studies have shown that the human-produced hormone molecules Epinephrine (Epi) and Nor-epinephrine (NE) activated the QseC/QseB system. We hypothesize here that (1) *F. novicida*, a model organism of *Francisella tularensis* synthesizes its own signaling molecule; and (2) it can be isolated from the Conditioned Media (CM). We showed that high concentration of CM inhibits bacterial growth demonstrating quorum sensing. We predicted that AI upregulates the production of biofilm that serves as a survival mechanism for the bacterium inside the environment. In order to purify the molecule from the CM, Boronate resin was used to first, purify epinephrine that served as a positive control; and second, to purify AI from the CM. A bacterial growth bioassay was done to confirm the activity of the purified molecule, having an inhibitory effect on the bacterial growth. The thin-liquid chromatography (TLC) and reverse-phase (C18) purification experiments did not confirm a similarity in the nature and the structure of potentially purified AI molecule to Epi and NE. Although the colorimetric test for catecholamine molecules confirmed the presence of the catecholamine in the purified fraction (after Boronate gel purification), the nuclear magnetic resonance (NMR) results showed dissimilarity in structure with Epi and NE as was noted by TLC and C18 results. We are continuing to elucidate the nature of the *Francisella* autoinducer.

253. **DXP synthase-catalyzed C-N bond formation: Implications for inhibitor design**

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The rising occurrence of microbial resistance to all currently available therapies has created a growing demand for new anti-infective drugs based on novel modes of action. Several opportunistic pathogens, including *Pseudomonas aeruginosa*, *Mycobacterium tuberculosis* and the malaria parasite, *Plasmodium falciparum* utilize the methylerythritol phosphate (MEP) pathway for isoprenoid biosynthesis. Isoprenoid production is essential, and the MEP pathway is absent in mammals; thus, the enzymes in this pathway are attractive targets for the development of new anti-infective agents. Currently, only a few inhibitors of non-mammalian isoprenoid biosynthesis are known. DXP synthase is the first step in this pathway and is known to catalyze the formation of a C-C bond in the production of deoxy-D-xylulose 5-phosphate (DXP) from pyruvate and D-glyceraldehyde 3-phosphate. In addition, DXP synthase catalyzes the early steps in thiamin diphosphate (ThDP) and vitamin B<sub>6</sub> biosynthesis. The similarity of this enzyme to the mammalian transketolase superfamily suggests that selective inhibition of DXP synthase may be a challenging endeavor. However, recent work has demonstrated that DXP synthase possesses a unique catalytic mechanism and structure, suggesting that development of selective inhibitors is possible. Here, we present a substrate specificity study that highlights DXP synthase-catalyzed C-N bond formation and reveals a remarkable affinity of the enzyme for naphthol-containing alternative substrates. Current efforts are focused on studying
structure-activity relationships for alternative substrate turnover and identifying important binding elements as a starting point for inhibitor design.

254. Antibacterial activity and synergy in chitosan-hops nanocomposites

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Chitosan, an inexpensive material prepared by partial depolymerization and deacetylation of chitin, was used to prepare nanoparticles, by ionotropic gelation. Sodium tripolyphosphate was used as crosslinking agent. Different conditions were used in the synthetic procedure. The influence of the pH on the solubility of chitosan and on the properties of the materials formed was studied as was the influence of ultrasonication. The size distribution in the materials obtained was determined and the zeta potentials were measured. The IR spectra of the particles were obtained too and discussed comparatively. Nanocomposite materials were prepared by ionotropic gelation using chitosan and hops extracts (lupulone and xanthohumol, respectively). Studies were conducted to determine the optimal conditions (pH, ratio polymer:crosslinker, ultrasonication) for the synthesis. The lupulone/xanthohumol content in the nanoparticles was determined by two methods (direct and indirect), using UV spectrometry. Size distribution, zeta potentials, and IR spectra were used to characterize the nanoparticulate materials. The antibacterial effect of the composite materials against *Bacillus subtilis* was assayed and compared to those of chitosan nanoparticles and starting chitosan, respectively. The synergistic effects found are discussed comparatively to those of other plant-based nanocomposites.

255. Thioamides as fluorescence quenchers: Minimalist chromophores to monitor protein dynamics

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Reducing the size of spectroscopic probes can increase the spatial resolution of fluorescence experiments on protein dynamics. We have shown p-cyanophenylalanine (Cnf) and backbone thioamides to be a distance-dependent fluorophore/quencher pair. We have used this pair to study the thermal denaturation of a Cnf/thioamide-labeled version of villin headpiece by fluorescence spectroscopy. We are currently exploring quenching interactions with other fluorophores and developing methodology to incorporate thioamides in large proteins. The small size of the thioamide probe opens the possibility of mapping conformational changes with a density far beyond what is currently possible.

256. Design and synthesis of novel hemoglobin crosslinkers based on 2,3 Diphosphoglycerate

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The quest for an effective blood substitute has been ongoing for several years. This search has only intensified recently with the recurrence of large scale civilian catastrophes. Hemoglobin (Hb) being the natural oxygen carrier inside the red blood cell, has been the preferred choice for developing blood substitutes. However, the implementation of hemoglobin as a blood substitute, suffers from two significant challenges. Firstly, when Hb is removed from the red blood cell, its tetrameric structure α1β1α2β2, breaks down into two smaller dimers, α1β1 and α2β2, which cause renal toxicity. Secondly, Hb increases its affinity for O₂, preventing the release of O₂ to the tissues. Loss of the natural allosteric effector of hemoglobin, 2,3-DPG, gives rise to the ineffectiveness of cell free Hb as an oxygen carrier. We have designed 1,2-bis phosphate esters as DPG mimics that should stabilize
the tetrameric structure of Hb within the DPG pocket while also imparting suitable oxygen transport properties.

257. Recognition and alkylation of DNA by PNA-QMP conjugates

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Quinone methides (QMs) are reactive intermediates generated by metabolic activation of several anti-cancer drugs. Electrophilic QMs can alkylate DNA and generate both reversible and irreversible adducts. To achieve target-specific alkylation, a PNA-QMP (peptide nucleic acid – quinone methide precursor) has been synthesized. Alkylation products between PNA-QMP and DNA were characterized by denaturing polyacrylamide gel electrophoresis (PAGE). PNA-QMP shows significantly more reactivity with a fully complementary DNA than with a one-base mismatched sequence. A reversible PNA-QM self-adduct has also been generated and shown to alkylate target DNA without external activation. Finally, a template DNA can direct alkylation of an adjacent strand of DNA by PNA-QMP. Several non-complementary bases at the terminal of this third strand are crucial for a high yield alkylation.

258. Criteria for Increasing Efficiency of Excess Electron Transfer in DNA

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Charge transfer processes in DNA are actively studied in various fields ranging from biological chemistry to electronics. While parameters affecting the efficiency of hole transfer have been extensively studied, equivalent investigations on excess electron transfer (EET) in DNA are not yet well resolved. The roles of charge recombination, as a competing process with electron migration, and the diffusional freedom of electrons during EET in DNA are reported. Charge recombination is reduced using selective electron donation to pyrimidines by 1-aminoanthracene (AA) as electron donor, in contrast to 1,5-diaminonaphthalene (DAN) that can donate to both purines and pyrimidines. Results show that AA is about 3-fold more efficient than DAN in inducing EET in identical dsDNA. Studies on a series of dsDNA with a terminal or internal electron donor reveal that the terminal donor with only one diffusion direction exhibits a 2-fold higher efficiency in transferring electrons in DNA. These findings may be used in the future to design more efficient EET systems in DNA.

Career Development Workshop

Organizer: J. Talisman

259. A career in chemistry—a personal journey

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Choosing a career in the chemical sciences is a life-decision; active management of this career-choice is an essential ingredient for success and satisfaction. Continuous learning, open-mindedness and flexibility towards new opportunities are also keys to career growth. The value of work-life balance cannot be over-emphasized, and must be nurtured and enjoyed in concert with career advancement. During this presentation, the author will offer tips and advice based on his own life journey traveling with a career in chemistry. His adventures, starting in high school in Chicago, proceeding through the universities, tracking a climb up the ladder in the federal government, proceeding to a stint in the private sector, and leading to the next steps will be graphically portrayed. Requisite knowledge, skills and abilities outside the traditional realm of the hard science of chemistry will be highlighted.
Innovative, low cost and replicable strategies to help students develop their career goals using web-based technologies

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The University of Maryland University College (UMUC), one of the 11 degree granting institutions under the USM umbrella offers a Master of Science in Biotechnology Studies. This 36 credit, online degree program is designed for open access and delivered through the UMUC proprietary online learning management system, WebTycho. The program is designated as a professional science master’s (PSM) degree and is aimed at training people to find employment in the biotechnology sector. In the PSM biotechnology program at UMUC we have developed two strategies to help our students develop a closer understanding of the workforce needs. In the first approach students are given the opportunity to work on projects sponsored by biotechnology companies, as part of their capstone course. As a result they get first hand experience working in a team on real life projects, as well as a closer look at the needs of the industry through interaction with the industry liaison. It also provides an avenue for the students to network with executives in companies and to establish a sustained professional relationship. The second approach is an online mentoring program where students in the PSM biotechnology program are offered the opportunity to apply to a biotechnology professional mentoring program. Once selected for the program the students are paired with mentors, who are biotechnology professionals from the industry, academia and the government. The uniqueness of this program is that it is offered to graduate students and utilizes web-based technologies for easy access and flexibility. With these two strategies the students are made aware of the workforce needs of tomorrow, learn to work in group projects that simulate work environments and develop a realistic set of professional goals with achievable action plans. These approaches position our graduates to have successful careers and are attractive because they are inherently discipline-independent and can be adapted by any program at any institution.

Cosmetic Science: An exciting alternative technical career path opportunity for chemists

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College graduates with a background in science have skills and expertise that are marketable in many areas of the Cosmetics Industry. Exciting, challenging opportunities for chemists, in particular, are available in both basic and applied research, designing and creating new finished products and their ingredients, as well as engineering the processes necessary for manufacturing operations. Jobs exist working for finished goods manufacturers, raw material suppliers, contract testing laboratories, academic institutions, and government laboratories. In each of these communities, advanced degrees may open more career options and potential for advancement. Information regarding job opportunities in the cosmetic industry and post-baccalaureate, degree-granting programs in cosmetic science is available through industry trade associations and professional societies such as the Society of Cosmetic Science (SCC) (http://www.scconline.org). Would you enjoy a career innovating, changing, and improving the products that consumers use daily for personal care to improve the quality of their lives? Where do your interest lie? Learn more in this presentation from the Society of Cosmetic Chemists!
262. Beyond the bench

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The Director of the JCVI Education Group, Lisa McDonald, has substantial experience developing course materials and content to present complex scientific methods and theories to groups of various educational backgrounds in an age-appropriate manner, including K-12 student groups and adults. As one of the founding employees at the J. Craig Venter Institute (formerly The Institute for Genomic Research, 1992), Ms. McDonald will discuss how her biochemistry background contributed to the Institute’s pioneering research. In addition, she was integral in the creation and development of the Education and Training Department in the late 90’s which she also led for five years. TIGR’s Education and Training Department, was committed to providing education and professional development courses in the field of genomics. Building upon TIGR’s expertise in genomics, professional development and education courses were designed to expose participants to hands-on applications and to disseminate current genomic knowledge. These programs included several technical training courses for internal employees, external participants, TIGR’s Summer Fellowship Program, teacher education and student education. Ms. McDonald oversees all aspects of the DiscoverGenomics! Science Education Program including summer internship program, organizational collaborations, curriculum development and grant submissions. She also serves on many local and state science education committees. Ms. McDonald will discuss the range of career opportunities in the field of genomics. In today’s growing genomic research fields, all STEM backgrounds are necessary for robust research in genomics.

263. Networking you way to your next position

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Over 70 percent of those landing positions claim networking was the key step. Over 50% of all positions are hidden from public view. Developing relationships that facilitate networking will be reviewed with examples that led to success. Tips for facilitating the process will be presented.

264. Careers in forensic chemistry: What they don’t tell you on CSI

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Over the past decade, several popular TV series have brought forensic science to the forefront of public consciousness. While these shows present forensics in an almost mystical light, forensic chemistry is, in reality, the careful application of sound analytical chemistry to questions likely to be brought before a court of law. It is, however, a rather different sort of analytical chemistry that might be found in more traditional sectors. In contrast to the academic world, forensic chemists are usually far more concerned with robustness and reproducibility than with elegance or novelty. When someone’s safety or liberty, or possibly even their life, is on the line, the chemist needs to be performing an analysis, not an experiment. On the other hand, forensic work often presents each analytical chemist with a far wider array of samples and analytical techniques than are seen by most individuals in the industrial world. Today may be an unknown white powder for identification, tomorrow may be a urine sample to be analyzed for drugs that might have been used to incapacitate a rape victim, and the next day could be a moldy ham sandwich to be analyzed for toxic heavy metals! Add to this the unique complications of performing work that must be presented within the framework of the adversarial legal system, and the result is a unique working environment.

This presentation will provide an overview of the realities of forensic chemistry and how they differ, both for better and for worse, from the fantastical images presented by the popular media. Attend-
ees will be provided with information about the types of careers and employers available to chemists within the field of forensics, and the educational expectations for entry into those career paths.

265. Careers in Technology Transfer and Business Development

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What is technology transfer / business development and what are the career opportunities in the field? What are the skills required and how does one acquire them? How can someone with a chemistry background truly pursue a non-traditional career such as this? These are the questions to be answered in this presentation from a (former) bench chemist and 30+ year ACS member.

In terms of background, the field of technology transfer itself is still relatively new and can trace its origins and rapid growth to the economic developments legislation of the early 1980s, a time when the US was looking to enhance its global competitiveness. The need for translating the ideas that have originated from academic labs into useful products (and the people to handle these tasks) is still with us and has only grown since then.

The technology transfer profession itself employs more than 10,000 professionals in the US with a fairly large number practicing their trade in the greater Washington, DC area. Career information is available from the sites of number of professional organizations such as www.autm.net, www.fedallabs.org or www.lesi.org along with formal training programs for scientists such as www.faes.org.

Graduate Research Opportunities in Government Laboratories

Organizer: J. Fourkas

266. Working with the National Institute of Standards and Technology: Research Collaborations, Funding, and Facilities Use

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The National Institute of Standards and Technology (NIST) is a historic, non-regulatory federal science agency. Its mission is broad—to promote U.S. innovation and industrial competitiveness by advancing measurement science, standards, and technology in ways that enhance economic security and improve our quality of life. NIST carries out its mission largely through its Laboratories, conducting research that advances the nation’s technology infrastructure and is needed by U.S. industry to continually improve products and services. The Material Measurement Laboratory (MML) is one of NIST’s laboratories; it supports the NIST mission by serving as the national reference laboratory for measurements in the chemical, biological and material sciences. In this talk, opportunities within MML for undergraduate, graduate, and postdoctoral research will be discussed. Several programs provide laboratory experience and financial assistance to qualified undergraduate and graduate students as well as post-doctoral research associates for the development of measurement methods, standards and data in a number of critical areas to the nation including advanced materials, biomedical and health technologies, electronics, energy, the environment, food and nutrition, physical infrastructure and safety and security. These opportunities offer many benefits to participants, including the opportunity to be co-advised and mentored by NIST’s measurement scientists, the opportunity to use world-class, often unique, equipment and facilities, and the chance to serve the country by addressing national measurement needs. Opportunities beyond student or post-doctoral research also exist; this talk will highlight how MML collaborates with partners in a variety of ways designed to meet a broad spectrum of needs. A key principle in the collaborative process is that both MML and its collaborators benefit from the relationship and the work contributes to advancing efforts to accom-
plish NIST’s mission. This talk will also provide information on MML’s external grants and cooperative agreement options, which are competitively awarded to universities and other institutions to conduct mission-relevant research and services, and on NIST laboratory facilities that are available for use for both proprietary and non-proprietary research. Key examples include the NIST Center for Neutron Research, which has user facilities for neutron-based measurements, and the Center for Nanoscale Science and Technology, which has user facilities for nanofabrication and nanoscale characterization equipment. The MML also takes an active role in promoting science and technology education through participation in a number of local programs hosted or sponsored by NIST on its campus in Gaithersburg, Maryland including a volunteer program for students in high school.

267. Detection of Low Concentration Analytes Using Gradient Elution Moving Boundary Electrophoresis

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The toxic effects of chronic exposure to low concentrations (parts per billion (ppb) or less) of many chemical species found naturally in the environment are well established. As a result, detection of these analytes with simple, field portable devices has been the focus of many efforts in the field of microfluidics. Gradient Elution Moving Boundary Electrophoresis (GEMBE) is a recently described technique for separation and detection of analytes at low concentrations. GEMBE is a counter flow electrophoresis technique that operates with a constant voltage and variable pressure. Currently, the limit of detection (LOD) of GEMBE is not low enough for some environmental analyses. In order to reduce the LOD, a novel stacking mechanism has been employed. Arsenic in water was used as a model system to demonstrate the feasibility of applying this technique to environmental analyses.

268. Raman spectroscopy for biodiesel determination

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The negative economic, political, and environmental effects of fossil fuels have created a need for suitable alternative to meet the worlds ever growing energy needs. Bio-fuels have come to the forefront in the list of possible competitors. Though standards for bio-fuel quality have been put in place, there currently is no standard for ensuring the quality of the bio-fuels. Furthermore, the techniques currently used to determine bio-fuel quality such as GC-FID are time consuming and expensive. Vibrational spectroscopy methods such as Near Infrared and Raman spectroscopy are both non-destructive and relatively fast techniques that are capable of identifying a given analyte. Herein we aim to develop a model capable of distinguishing the characteristics of bio-fuels using multivariate analysis. Furthermore, we aim to determine the feasibility of using Near infrared (NIR) and/or Raman spectroscopy for quality assessment, profiling, and sourcing of bio-fuels based on these models.
269. Partnership for Cancer Technology between the University of Maryland and the National Cancer Institute

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The Partnership for Cancer Technology between the University of Maryland and the National Cancer Institute brings together the expertise and resources in the mathematical sciences, physical sciences, and engineering at the University of Maryland College Park, with basic, clinical, and translational research expertise of the National Cancer Institute to solve the most pressing problems in cancer research. In this talk an overview over current joint projects, including specific examples of transfer of expertise will be presented. Approaches to developing collaborations and to finding mentors at the National Institutes of Health will be discussed.

Emerging Problems in the 21st Century
Organizer: P. Deshong

270. Current status in understanding climate and climate change prediction

**Joyce E. Penner**\(^{(1)}\), penner@umich.edu, 2455 Hayward St., Ann Arbor MI, United States. (1) University of Michigan, Ann Arbor, United States

In this talk I will review what we know about climate change, the causes of climate change and its attribution. I will also discuss observed changes in extremes and whether these can be attributed to anthropogenic causes. Finally, I will end with what we understand might be in store for us in the future as given by climate change projections.

271. The re-emergence of infectious diseases

**Clifton E. Barry**\(^{(1)}\), clifton_barry@nih.gov, 9000 Rockville Pike, Bethesda MD, United States. (1) National Institutes of Health, United States

Infectious diseases have afflicted mankind since the dawn of time and exact a huge toll on our civilization. Unluckily that toll is mostly borne by those least able to bear it, poverty and death from infectious disease are directly linked. Virtually all of the “bottom billion” of earth’s inhabitants are infected with at least one infectious disease. Migration, immigration and transcontinental travel fuel the spread of these diseases to the developed world where they are confronted by modern medicine – typically in the form of antibiotics or antivirals. As we apply our arsenal of drugs more and more frequently to contain outbreaks of the major diseases evolutionary pressure is placed on these organisms to develop more and more drug-resistance. Few pharmaceutical companies have invested in the development of novel agents to combat a potential epidemic of drug-resistant infectious diseases. Compared with chronic disease with life-long therapy, anti-infectives, with rapid cures, offer a generally poor return on investment. Compounding the problem the tools of modern structure-based drug design combined with genomics have been a dismal failure when applied to complex microbes leading many companies to abandon such efforts completely. Since the 1960s only a handful of chemical scaffolds have dominated anti-infectives and the 40 years between 1960 and the introduction of the oxazolidinones in 2000 are often dubbed “the innovation gap”. We are a long way from understanding why genomics has failed in anti-infectives drug development but if we want to avoid extending the innovation gap to include our own scientific generation we must redouble our efforts to try to bridge chemistry and genomics.
272. Energy issues in the 21st century
Eric D. Wachsman(1), ewach@umd.edu, Jeong H. Kim Engineering Building, University of Maryland, College Park MD, United States. (1) Energy Research Center, University of Maryland, College Park, United States

Our quality of life, standard of living and national security depend on energy. Growing third world economies combined with finite resources are putting a tremendous strain on the availability of energy and we will have no choice but to transition to a diverse set of energy resources in the 21st Century. Therefore, a strong, balanced energy portfolio, based on the most efficient use of our natural resources while minimizing our dependence on imported energy is critical to the U.S. The science and technology being developed to address this will be reviewed. How rapidly we incorporate renewable energy resources in the mix and whether we create the resulting companies and jobs in the U.S. depends on the economics relative to conventional resources. How the economics plays out depends on whether the public believes in climate change science and puts a price on carbon.

Chemical Genomics
Organizer: R. Guha

273. Analyzing protein-protein interactions for annotation prediction
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Determining a protein’s function and whether it plays a role in disease is a fundamental bioinformatics challenge. Protein-protein interaction networks are an increasingly useful data source from which to computationally tackle this problem. I will describe several novel computational techniques that have proven useful for associating proteins with functions and diseases using protein-protein interactions. In particular, I will focus on an approach that uses the combinatorial optimization problem of metric labeling to propagate labels within the network (joint work with Emre Sefer). This technique outperforms other state-of-the-art methods, is computationally efficient, and provides a natural way to incorporate similarities between possible annotations.

274. Merging biological and chemical spaces using machine learning approaches.
Huzefa Rangwala(1), rangwala@cs.gmu.edu, 4400 University Dr. MS 4A5, Fairfax VA 22030, United States. (1) Department of Computer Science, George Mason University, United States

With the advances in high-throughput and high-content screening approaches, we have observed the ever-increasing use of chemical genetics, which involves altering the function of a protein by use of small organic molecules. Small organic molecules (a.k.a. ligands) can bind to different proteins and modulate (inhibit/activate) their functions. Understanding these interactions provides insight into the underlying biological processes and is useful for designing therapeutic drugs. Small molecules can work rapidly and reversibly, can modulate a single function of a multifunction protein, and can disrupt protein-protein interactions. In this work, we have developed machine learning based approaches that allow us to analyze the information associated with proteins and their interacting molecule partners (protein-ligand activity matrix). The underlying hypothesis of our approach is that by extracting information from protein-ligand activity matrix, we are drawing bridges between the structure of chemical compounds (chemical space) and the structure of the proteins and their functions (biological space).

We present a novel feature enriched co-clustering method (Wang, et al. 2011) that co-clusters the relational data obtained from the activity matrix, along with protein sequence features along with
molecule’s topological features. Co-clustering is an important technique for mining relational data, especially when data are sparse and high-dimensional. It allows for simultaneously grouping of different kinds of proteins and molecules involved in a relation. We specifically evaluated our approach on a dataset where the proteins were restricted to be G-protein coupled receptors, which are important therapeutic targets as well as a set of proteins that came from a general class of enzymes.

We also present an approach that utilizes the activity information from multiple protein targets for improving the predictive performance of structure-activity-relationship (SAR) models (Ning, Rangwala and Karypis 2009). Specifically, our work first identifies those set of protein targets that are related, and then various machine-learning based approaches extract the activity information associated with the related targets to train better SAR models. Our method relies on defining relationship between protein targets by extracting sequence-based features, but also tying in information associated with the structure of the chemical molecules. For utilizing the information we developed methods based on principles of semi-supervised, multi-task learning and ensemble approaches. Our evaluation based on an information-retrieval metric shows that the multi-assay based approaches are superior in comparison to the base line SAR models. We also compare the performance of our multi-assay based approach to methods that use a chemogenomics-based approach.

These methods developed, greatly increase the set of proteins that can be selectively modulated via small organic molecules. This expands the various biological processes that can be investigated via chemical genetics approaches, and allows researchers to use chemical genetics techniques to gain insights on the mechanisms of action associated with certain phenotypes.

Bibliography


275. FDA/USP Substance Registration System (SRS) as an informational bridge between chemistry and biology

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The primary goal of the FDA/USP Substance Registration System (SRS) is to unambiguously define all substances present in regulated products. Once a substance has been defined, SRS assigns a strong identifier that is permanently associated with the substance. SRS defines a substance as any matter that has a discrete existence, irrespective of origin, which may be biological or chemical. Substances can be single well-defined chemical entities containing a definite molecular structure, synthetic (e.g., isomeric mixtures) or naturally-occurring (e.g. conjugated estrogens) mixtures of chemicals, or materials derived from plants, animals, microorganisms or inorganic matrices that are not definable by a single or limited number of molecular structures. Substance definitions are based on molecular structure or other immutable properties of a given material. Purity, physical form, and method of production are not considered when defining substances. This presentation will describe how materials at different levels of complexity are defined by SRS.
276. Cross validation of the biomedical data from disparate chemogenomics databases: Application to the serotonin receptor 5-HT1A ligands

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In the past fifteen years, innovative technologies that enable rapid synthesis and high throughput screening of large libraries of compounds against a wide range of biomedical targets/pathways. As a result, there has been a significant increase in the total number and size of annotated chemogenomics databases that become available to the academic research community. In order to validate the congruence of data from disparate sources, we selected the 5-Hydroxytryptamine Receptor Subtype 1A (5-HT1A) ligands as the probe system and retrieve the datasets from NIMH Psychoactive Drug Screening Program (PDSP) Ki database (105 binders/61 non-binders), World of Molecular Bioactivity (WOMBAT) database (69 binders), and PubChem confirmatory assays (46 agonists/antagonists) (PubChem AID: 613, 718, 755). Three advanced methods of Quantitative Structure-Activity Relationships (QSAR) modeling $k$-Nearest Neighbor ($k$NN), Random Forest (RF) and Support Vector Machines (SVM), were employed for model building with external five-fold cross validation for each dataset. Highly predictive models were generated from the datasets derived from PDSP and WOMBAT databases and the inter-database cross validations between the two were consistent, e.g. the Correct Correlation Rate (CCR) is as high as 0.95 when predicting 69 WOMBAT binders using models from PDSP dataset. However, the cross validations on the PubChem data from the other two databases were not consistent and showed low accuracies. Fourteen putative hits were predicted to be non-binders by all three methods and were confirmed later by our experimental collaborators.

277. Role of C Terminus of Bacteriorhodopsin in protein stability

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Bacteriorhodopsin (bR) exists as a 7-helix trans-membrane protein with a 23-residue sequence C-terminus (CT) exposed to the aqueous intracellular environment. The presence of the CT has been shown to contribute to the overall stability and function of bR; however, to date XRD crystal data indicate that the CT lacks a well-defined equilibrium structure. All-atom MD simulations of the CT in aqueous ionic solution have been undertaken to help establish the likely structure of the CT as a function of solvent salt concentration. High temperature simulated annealing was used to mitigate initial state effects as well as to promote sampling of a broader space. All MD simulations included explicit water, a host lipid membrane matrix and solvent ions. The solvent accessibility and root-mean-square deviations of the CT in equilibrium are presented, which show that the overall stability of the transmembrane portion of bR is enhanced by interactions with the CT. The investigations include a comparison of CT-bR interactions with the CT bound and unbound to bR.

278. Simple Method for Calculating log P of Environmentally Interesting Compounds

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The commonest descriptor in environmental studies is log P. Many methods of calculating it have appeared in the last 30 years. Mannhold et al. have reviewed these and proposed their own: (1) $\log P = 0.11(\pm 0.007) N_c - 0.11(\pm 0.0017) N_{het} + 1.46(\pm 0.027)$ (1) which was very effective in modeling the Pfizer database of 95,809 compounds. NC is the number of C atoms and NHet the number of atoms other than C or H in the compound. Clearly an increase in NHet results in a decrease in log P while an increase in NC has the opposite effect. We have successfully correlated log P values for M
Food Safety
Organizers: K. Morehouse, B. Yakes

280. Food safety modernizatoin act: overview of the new law and impact on laboratories.
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Congress enacted the most sweeping changes to food safety law in more than 70 years on January 4th, 2011. GMA worked closely with legislators to craft the FDA Food Safety Modernization Act (FSMA) and will work closely with the FDA to develop rules and guidance to implement the provisions of this new law. To help the food industry understand the impacts of this new legislation, Shannon Cole will provide an overview of the FSMA. The agenda includes an overview of the major provisions of the new law and how they will affect the food industry, including:

* What new responsibilities will food companies face?
* What import controls will be in force?
* What enforcement powers will FDA have?
* What fees will food companies and importers have to pay?

Furthermore, an overview of the implementation strategy shared by FDA and the path forward within the GMA membership will also be discussed.
281. FDA/USP Substance Registration System (SRS) as a tool for codifying food ingredients

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An important step toward protecting public safety is to identify what is in a product. The primary goal of the FDA/USP Substance Registration System (SRS) is to unambiguously define all substances present in regulated products. Once a substance has been defined, SRS assigns a strong identifier that is permanently associated with the substance. SRS substance definitions are based on molecular structure or other immutable properties of a given material. Food ingredients have been particularly challenging to codify because ingredients may be anything from single molecular entities to entire organisms. SRS provides a definitional structure of sufficient breadth to accommodate sucrose, sugar kelp, and anything in between. This presentation will offer examples of SRS definitions for foods, food additives, and dietary supplements.

282. Headspace Solid Phase Microextraction-Gas Chromatography Mass Spectrometry (HS-SPME-GCMS)-Analysis of Food Additives and Contaminants

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One of the most time consuming steps in the analysis of food contaminants is sample preparation. Over the past 15 years, several new sample preparation techniques have been introduced which allow sample clean up and enrichment in a single step. One of the most widely used of these extraction methods is headspace solid phase microextraction (HS-SPME). In HS-SPME a fused silica fiber with a polymer coating is exposed to the headspace of a sample, allowing analytes to partition among the sample matrix, headspace and the fiber surface. After a set extraction time the fiber is inserted into the injection port of a GC and the analytes are thermally desorbed. This technique is automated and is directly compatible with most GC instruments. In addition to reducing the personnel resources required for sample processing, these autosamplers increase reproducibility of the extractions while minimizing analysts’ exposure to potentially toxic analytes. Over the past 5 years CFSAN has used HS-SPME-GCMS to develop methods for food defense (tetramine), food additives (vanillin), contaminants (PAHs), adulterants (coumarin) and markers of degradation (hexanal). An overview of the research projects, along with analytical results, will be presented.

283. QuEChERS sample preparation: Advancements and modifications in the methodology

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The QuEChERS approach was validated for the analysis of multi-residue pesticides in fruits and vegetables. Applying this sample preparation technique can be very advantageous specifically with GC/MS, GC/MS/MS and LC/MS/MS analysis. Since the QuEChERS inception it has been applied to a variety of different matrices and compounds well beyond pesticides. Employing this sample preparation technique in new matrices and for the analysis of compounds other than pesticides requires an understanding of the parameters associated with this technique. We will discuss the basics associated with the QuEChERS technique and various parameters and how to implement the QuEChERS technique in new or different matrices and for a variety of compounds.
284. **LC-MS/MS detection of glycidyl esters and 3-MCPD esters in edible oils**

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3-Monochloro-1,2-propanediol (3-MCPD) esters and glycidyl esters are chemical contaminants formed during the processing of edible oils. Through hydrolysis of the ester linkages, free 3-MCPD and glycidol, respectively, would be released, both of which are known to induce tumors in rodents. The compounds have proven to be difficult to detect and quantitate using conventional analytical methodology. Currently the most widely used method is the Deutsche Gesellschaft für Fettwissenschaft (DGF) standard method C-III 18 (09). It does not directly measure the fatty acid esters of 3-MCPD or glycidol which are actually formed during edible oil processing and likely differ in toxicity from free 3-MCPD and glycidol. It is clear that a quantitative method which detects intact 3-MCPD and glycidyl esters is needed.

The LC-MS/MS method described in this presentation detects and quantitates intact 3-MCPD and glycidyl esters in edible oils at concentrations as low as 100 ppb. The method involves a rapid SPE cleanup and is applicable to both solid and liquid food products. Quantitative analysis of the extracts utilizes liquid chromatography with tandem mass spectrometry (LC-MS/MS) detection using atmospheric pressure chemical ionization (APCI). The method is rugged, sensitive and specific and allows for the direct determination of fatty acid esters of 3-MCPD and glycidol in a method suitable for regulatory analysis.

285. **Determination of siloxanes in silicone nipples and potential migration to milk/formula products**

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The determination of siloxanes in silicone nipples and the potential migration to milk/formula plays an important role in the assessment of infant exposure to these compounds. In this on-going study, a gas chromatography mass spectrometry selective ion monitoring (GC-MS-SIM) method was developed to determine three cyclic siloxanes; octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), dodecamethylcyclohexasiloxane (D6) and three linear siloxanes, octamethyltrisiloxane (L3), decamethyltetrasiloxane (L4), dodecamethylpentasiloxane (L5) in silicone products. The limit of quantitation (LOQ) of the six siloxanes ranges from 5 µg/kg (D4) to 15 µg/kg (L3). Coupled with pressurized liquid extractions (PLE), the GC-MS-SIM method was used to screen for the six siloxanes in various silicone feeding nipples collected from local stores. No linear siloxanes were detected in the silicone nipple samples analyzed. The three cyclic siloxanes (D4, D5 and D6) were detected in all samples with concentrations ranging from 0.5 mg/kg to 300 mg/kg. Because of these siloxane concentrations in nipples, there is a need to evaluate the migration from nipples to milk/formula. Therefore a liquid extraction and dispersive clean-up procedure was developed for cyclic siloxanes in milk/formula. The procedure used a mix of hexane and ethyl acetate (1:1, v:v) as extraction solvent and C18 as the dispersive clean-up sorbent. The mean percent recoveries (recovery%±RSD%, n=4) from the spiked formula at the 50, 100, 200, 500 and 1,000 µg/kg concentrations were 88±8, 95±5, 87±4, 94±10, and 97±12, respectively. Using this extraction procedure and the GC-MS-SIM method, we are investigating the migration potential of cyclic siloxanes from nipples into milk/formula.
286. Development of an isotope dilution assay for the regulatory analysis of the allergenic milk protein α-S1-casein utilizing an intact $^{15}$N-labeled protein internal standard

Peter F. Scholl(1), peter.scholl@fda.hhs.gov, 5100 Paint Branch Parkway, HFS-707, Room BE-006, College Park MD 20740, United States; G. Asher Newsome(1); John Callahan(1). (1) Center for Food Safety and Applied Nutrition, U.S. Food and Drug Administration, College Park MD 20740, United States

Food mislabeling or contamination by processing equipment can result in exposure to allergens that provokes anaphylactic shock in susceptible individuals. Approximately 2% of adults and 5% of children in the USA exhibit allergies against milk, nuts, eggs, seafood, or gluten and 30,000 deaths per year are attributed to allergen exposure. The Food Allergen Labeling and Consumer Protection Action of 2004 (FALCPA) requires that food containing major food allergens declare them on the package label. However, threshold milk allergen levels have not been established. Sensitive immunochemical methods are used to detect allergens in the ppm range but more specific methods may be of complementary use to reduce false positive detection rates in complex food matrices such as baked goods. Mass spectrometry is a more specific detection method and has been used to screen foods for the presence of milk allergens; however, it has not been used to rigorously measure the concentration of α-S1-casein in food samples. Use of intact $^{15}$N-labeled α-S1-casein protein and $^{15}$N-/$^{13}$C-labeled peptides is described to develop a multiple reaction monitoring mass spectrometric method for the quantitative analysis of α-S1-casein and the multiplexed detection of other allergenic casein and whey proteins. Assay performance is demonstrated using non-fat dry milk-incurred baked cookies. Current efforts are directed at enabling routine milk allergen detection below the 5ppm level. This analytical approach can be generalized and extended to other food allergens. The α-S1-casein assay may facilitate the establishment of food allergen thresholds and enforcement of FALCPA by providing a highly specific and sensitive method for the detection of milk protein allergens.

287. Top-down mass spectrometry for the rapid identification of strain specific bacterial proteins

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Faster and more effective methods for bacterial assessment are becoming increasingly relevant. Intact protein expression profiling by LCMS is a powerful tool for bacterial strain differentiation. However, transfer to field usable assays or monitoring of drift in these species requires identification of marker proteins. The availability of predicted proteins from a rapidly expanding database of bacterial genomes affords the possibility of developing tools in which partial protein sequence information obtained from top-down mass spectrometry can rapidly identify strain specific proteins. Combined with the associated molecular weight information, the approach can identify variations in protein structure that are related to bacterial strain differences. In addition, comparative proteogenomics of closely related bacteria by top-down MSMS allows us to go beyond identification of possible cross-serovar orthologs. Access to intact protein masses, HPLC retention times, and site specific MSMS data provides insight into specific mutations, PTMs, start site errors and signal peptide cleavages that are often poorly annotated in sequence databases.
288. Tolerance of bacteria against several series of triorganotin compounds

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Several series of triorganotins in which triorganotin compounds were incorporated into modified fragments of pyretheroids, as well as a host of commercially available triorganotins, were screened against the bacteria *Escherichia coli* (*E. coli*) and *Bacillus substilis* (*B. substilis*). The three series included triorganotin 3-(p-chlorophenyl)-3-methylbutyrates, triorganotin 2,2-dimethyl-3-(2-methyl-1-propenyl) cyclopropane-carboxylates and triorganotin 2,2,3,3-tetramethyl-cyclopropane-carboxylates. Preliminary results indicated that *E. coli* were more tolerant to the three series of modified triorganotin pyretheroids than *B. substilis*, based on the averages calculated for the three series of complexes. However, the triethyltin derivatives were the most effective toxicant in each series.

289. Expanding the Range of Polyolefins through Living Coordinative Chain Transfer Polymerization

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Recently, a non-chain-terminating, rapid and reversible chain-transfer process has been introduced to living alkene polymerization that is mediated by homogeneous single-site transition-metal catalysts. This strategy, termed living coordinative chain transfer polymerization (LCCTP), overcomes the ‘one-polymer-chain-per-metal’ limitation on polymerization yields by employing excess equivalents of a main-group metal alkyl as surrogate metal chain-growth sites. The extension of this strategy through addition of a chain-transfer mediator enables the scalable production of precisely controlled precision polyolefins (POs), as well as end-group functionalized PO-based materials. In addition, a broad spectrum of monodisperse polyethylene copolymers with programmable modulation of comonomer compositions have been obtained using rapid and reversible chain-transfer between ‘tight’ and ‘loose’ ion pairs generated from a single cationic transition-metal catalyst.

290. Effects of Strong Donor/Acceptor Electronic Mixing in Ruthenium(II) poly-pyridyl Complexes Manifested in their Spectroscopic and Electrochemical Properties and Supported by Computational Methods.

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The lowest energy metal to ligand charge transfer (MLCT) absorption bands found in ambient solutions of [Ru(L)2 (bpy)2 ]+ complexes (where (L)n are substituted acetylacetonate, halide, am(m) ine, etc.) consist of two partly resolved absorption envelopes. TD-DFT modeling of the HOMO□LUMO transition of [Ru(L)4 bpy]m+complexes indicates that it is too weak to be detected and occurs at significantly lower energy (about 3000−5000 cm−1 ) than the observed MLCT absorptions. Since the chemical properties of MLCT excited states are generally correlated with the HOMO and/or LUMO properties of the complexes, such very weak HOMO□LUMO transitions can complicate the use of spectroscopic information in their assessment.
291. Hydrogenation of Quinoline by Palladium nanoparticles on MgO

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Petroleum-derived transportation fuels are a major source of sulfur and nitrogen emissions in the environment. Catalytic hydrogenation is a useful method to reduce the aromatics, as well as to remove sulfur and nitrogen from fossil fuels through hydrodesulfurization and hydrodenitrogenation. However, current technologies are unable to achieve the required lower levels of these compounds.

We have synthesized nano-structured catalysts composed of Pd particles immobilized on MgO, particularly suited for the heterolytic splitting of hydrogen and ionic hydrogenation mechanisms. Characterization was performed by Transmission Electron Microscopy (TEM) and Powder X-ray Diffraction (PXRD). These new materials catalyze the hydrogenation of quinoline under moderate conditions.

292. Precision Polymers from Living Coordinative Chain Transfer Co- and Terpolymerization of Ethene, Norbornene and α-Olefins

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With societal dependence on polyolefins (POs) steadily increasing, considerable effort has been devoted to the copolymerization of commodity volume monomers, ethene (E) and propene (P), with a-olefins and cyclic comonomers, such as norbornene (NB). In this regard, cyclic olefin copolymers (COCs), constituting varying E-NB copolymer compositions, are known to exhibit high transparency and glass transition temperatures (T_g), good processibility, low dielectric constants, biocompatibility, and stability against chemical degradation making them perfect candidates for use in a broad range of applications in optical, electric and medical fields. Given the industrial interest in COC materials, we have investigated the living coordinative chain-transfer copolymerization of E and NB as a practical route for the scalable synthesis of bulk quantities of precision polyolefins based on poly(ethene-co-norbornene) and poly(ethene-co-norbornene)-b-poly(ethene-co-α-olefin). The results of these studies reveal that, by adjusting concentrations of the ZnEt_2 chain transfer reagent and the comonomer NB feed ratio, LCCTP can be employed to modulate the copolymer composition and microstructure of these poly(ethene-co-norbornene) and poly(ethene-co-norbornene)-b-poly(ethene-co-α-olefin) materials over a broad range.

293. Synthesis, electrochemical and computational studies of (η^4-C_5Ph_4=O) Fe(CO)_2L

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For hydrogen to become a viable alternative energy carrier an abundant, inexpensive electrocatalyst is needed. Iron provides an avenue of exploration as a metalcenter in such catalysts. To gain a greater understanding of the catalytic properties of hydrogen-evolving organometallic iron electrocatalysts, the series (η^4-C_5Ph_4=O)Fe(CO)_2L (L=PR_3, P(OR)_3, R=Ph, Me, Et) was synthesized. DFT computational investigation has been used to rationalize the observed structural and electronic properties. Electrochemical studies show that (η^4-C_5Ph_4=O)Fe(CO)_2 is able to modestly catalyze the formation of H_2 from weak acid sources. Additionally, scan rate studies reveal a suspected ketone-protonation mechanism in the presence of acid.
294. Design aspects of organometallic electrocatalysts for hydrogen production

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Current methods of hydrogen production as an energy carrier are both expensive and environmentally harmful. The use of organometallic electrocatalysts based upon cheap metals and utilizing structural motifs inspired by natural systems could provide a solution. One such electrocatalyst, CpFe(CO)₂I, has been studied with electrochemistry in the presence of various proton donors. This system is amenable to substitution reactions where one carbonyl group is removed and replaced by various phosphine and phosphite ligands. The remaining CO ligand IR stretching frequency is used as a probe for the electron density on the central iron atom and comparisons to DFT computation are made. This systematic study of electron density upon the central metal is instructive, as it is thought that such electron density plays a role in the rate limiting step of many organometallic electrocatalyst systems.

295. Design of a “greener” oxidation process for the synthesis of polyol alkanoic acids

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Selective oxidation of carbonyl groups to their corresponding acids in compounds containing both alcohol and aldehyde groups is of growing interest in the specialty chemicals and pharmaceutical industry. Compounds containing alcohol and carboxylic acid functional groups are used in waterborne and powder coating systems as well as in the formation of dendrimers. These types of compounds impart water solubility of the coating system into the polymer, and therefore allow for the formulation of lower VOC or more environmental friendly coatings.

An example of a compound that is of interest to both the coatings and pharmaceutical industries is dimethylolpropionic acid (DMPA). Currently DMPA is produced by the stiochiometric peroxide oxidation of the dimethylolpropanal (DMPAL). The current reported synthesis and production of DMPA is carbon inefficient, requires a lot of energy and is not catalytic. A more economical and efficient synthetic route to DMPA® and these types of compounds, in general, using air or an oxygen atmosphere in the presence of transition metal catalysts is under investigation. Initial results to date indicate the successful selective oxidation of the aldehyde group under mild conditions using transition metals. Nickel (II), copper (II), iron (II), iron (III) and manganese (II) salts and complexes have been investigated to determine the optimal catalyst and reaction conditions for the development of a mild air oxidation process for DMPA and other desirable polyol alkanoic acids.

296. Synthesis of ferrocenyl alcohols as precursors to acrylate and methacrylate monomers

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An extension of a convenient one-step synthesis to prepare 1-ferrocenyl, 2-propanol, 1-ferrocenyl,2-butanol, and 2-ferrocenyl 1-phenylethanol. The alcohols serve as precursors in the preparation of the...
acrylate and methacrylate monomers which may be used to make ferrocenyl polymers. Compounds were characterized by Nuclear Magnetic Resonance (NMR) Spectroscopy, Mass Spectroscopy (MS) and X-ray crystallography.

297. The facile fabrication of PtSn₄ and Ir₃Sn₇ intermetallic nanoparticles from bimetallic Zintl clusters

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The synthesis and characterization of bimetallic Zintl clusters has been of particular interest to the growing field of nanotechnology. Despite their importance, much is still unknown about the stability and dynamic properties of important known reforming catalysts in the oil and gas industries, such as PtSn₄ and other tin alloys. PtSn₄ is believed to have high catalytic activity in gas reforming, but is difficult to prepare and isolate due to the formation of the other known Pt-Sn phases such as PtSn and PtSn. Research leading to an advantageous fabrication method of PtSn₄ and Ir₃Sn₇ has been studied, giving facile fabrication from Zintl cluster precursors. Ir₃Sn₇ and sub-10 nm PtSn₄ nanoparticles have been fabricated from the bimetallic clusters [Sn₉Ir(cod)]²⁻ and [Pt₂Sn₉(PPh₃)]²⁻ respectively, giving ordered intermetallic nanoparticles for the first time. The nanoparticles were characterized via TEM and X-ray diffraction methods.

298. Use of di(p-hydroxybenzylidene)acetone palladium(0) compounds in the synthesis of organopalladium complexes

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Palladium dibenzylidineacetone (dba) complexes, such as tris(dibenzylideneacetone)dipalladium(0) (Pddba₃), are common sources of palladium in the synthesis of many different organometallic compounds. However, complications can arise when purifying the desired product from the released dba ligands. Past research has shown that when hydroxyl groups are placed on the benzene rings of the dibenzylideneacetone ligands it changes the solubility both the precursor and the dba ligands, making purifying the desired products more readily achieved. In this paper, we present an improved synthesis of a di(p-hydroxybenzylidene)acetone palladium(0) complex, as well as the use of this complex as a palladium source in the synthesis of a variety of catalytically interesting palladium compounds.

299. Design and synthesis of chelating chiral phosphine compounds as potential ligands for catalysis

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The development of catalysts for asymmetric synthesis with n-alkanes as starting material is of great importance and has significant applications in the petroleum and pharmaceutical industries, including the use of alternative feed stocks to produce new and existing products, the development of new materials, and the synthesis of pharmaceuticals and other bioactive compounds. Recently, Goldman, Brookhardt and others have demonstrated that “pincer-type” ligand metal complexes are useful catalysts in the formation of aromatic hydrocarbons. It has been suggested that the reactivity of these catalysts was due to the sterics of the phosphorus atom, while others contended that the metal –phosphorus plane was the key factor on how substrates coordinate to the metal center. The manner in which the substrate binds to the metal determines the stereochemistry of the product; therefore, varying the
substituents on the phosphorus atom and/or the phosphine ligand backbone to widen the substrate metal coordination site should have a dramatic affect on the stereochemistry.

Research efforts, to date, have focused on varying the nature of the phosphine ligand backbone in order to constrict or widen the coordination site for the substrate to bind to the metal in an attempt to affect the stereochemistry of the resulting chemical transformation. Effort has been made to synthesize chiral, non-racemic chelating phosphine ligands or “pincer-type” phosphine ligands that could form metal facial-isomers, which should have a large impact on the way the substrate approaches and binds to a metal center. The design and synthetic route to the target molecules will be presented herein.

300. Synthesis, characterization, and anticancer effects of a 4-hydroxy pyridine derivative of NAMI-A

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The ruthenium-based anticancer drug NAMI-A and many of its derivatives have been extensively studied extensively in recent years due to their remarkable ability to inhibit the growth of metastatic tumor cells. The mechanism, though still unclear, is believed to be related to the hydrolysis process in which the chloride ions connected to the central ruthenium are replaced by hydroxyl groups in a stepwise manner. This process is subject to conditional influences such as pH and buffer composition, among others. Most NAMI-A derivatives possess an imidazole-based axial ligand. We have discovered that a NAMI-A derivative containing 4-hydroxypyridine in place of imidazole hydrolyzes significantly faster than NAMI-A under various pH conditions, suggesting that it may function as a more effective antimetastatic drug than its parent compound. The compound, (OHPy)[dmso-transRuCl4-OHPy], was synthesized using similar technique to that for NAMI-A and characterized using IR, UV-vis and CHN analysis. Gaussian was used to simulate the geometric configuration of the hydrolyzed molecule using DFT and unrestricted B3LYP approaches, and the simulated IR spectrum was compared with the experimental data obtained. Furthermore, the compound’s ability to inhibit growth of metastatic tumor cells was evaluated using the LL/2 mouse lung cancer cell line.

301. Synthesis of Low-Coordinate Manganese Clusters

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Photosystem II uses a tetranuclear manganese structure to achieve the efficient oxidation of water. Current synthetic models feature 6-coordinate manganese with multidentate ligation, which stabilizes high oxidation states, and leaves no coordination site for water to bind. For viable biomimetic chemistry, this project focuses on the synthesis of 4-coordinate manganese-oxo clusters with sterically bulky terminal ligands. The development of such low-coordinate clusters offer promise for bet-
ter biomimetic models. Using oxidation reactions with Mananganese compounds and bulky ligands, low coordinate clusters were attempted to be made in nitrogen-rich environment. Prepared clusters were characterized by NMR and single-crystal X-ray diffraction techniques.

302. Ruthenium nanoparticles supported on Poly(4-vinylpyridine) as catalyst for hydrogenation of aromatics and evidence for a dual site mechanism

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Background and Aims Fossil fuels currently provide over 80% of all the energy consumed in the US, according to the DOE.1 Reports by the IEA indicate the continued predominance of fossil energy sources in 2030.2 Even with aggressive development of renewable and nuclear technologies, it is likely that the nation’s reliance on fossil fuels will increase over at least the next two decades.3 Current legislation imposes severe limits on the amounts of aromatics, sulfur and nitrogen in fuels, which is difficult to achieve with current refining technologies. Catalytic hydrogenation may play an important role in the production of cleaner fuels as a key step in HDS and HDN processes but conventional catalysts require drastic conditions and/or are easily poisoned.4 Therefore, there is a need for new efficient catalysts for hydrogenation reactions relevant to the production of cleaner fossil fuels.

The object of this project is to synthesize and characterize ruthenium nanoparticles (RuNPs) immobilized on poly(4-vinylpyridine) (PVPy) and to study their catalytic properties in the hydrogenation of relevant aromatic compounds representative of diesel and gasoline components.

Our hypothesis is that the nanostructured Ru/PVPy catalyst can promote heterolytic splitting of hydrogen and efficient ionic mechanisms in the hydrogenation of aromatics, thereby avoiding catalyst poisoning. Such mechanisms are common in solution,5 but are extremely rare on metallic surfaces.

Catalyst Synthesis and Characterization We have prepared supported RuNPs by performing the borohydride reduction of RuCl₃ in the presence of PVPy.6 The new material has been characterized by transmission electron spectroscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

Catalytic Tests and Mechanistic Insights Ru/PVPy has proven to be a new versatile catalyst for hydrogenation of a variety of arenes and N-heteroaromatics representative of components of petroleum-derived fuels. Recyclability studies show that the catalyst may be re-used for at least three cycles without any appreciable loss of activity. The effect of solvent polarity and addition of external acid or base, substrate competition experiments and selective thiophene poisoning tests suggest the existence of two distinct active sites, involving conventional homolytic hydrogen splitting and rare heterolytic hydrogen splitting on metallic surfaces.

References:


### 303. Small Molecule Activation by Group 6 M(IV) Terminal Oxo and Imido Complexes Supported by the Monocyclopentadienyl, Amidinate Ligand Set

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Dinitrogen complexes, \{Cp*M[N(iPr)C(Me)N(iPr)]_2(η^1:η^1-μ-N_2) \} (Cp* = η^5-C_5Me_5; for M = Mo (1) and W (2)), were used as M(II, d^2) synthons to quantitatively provide the corresponding M(IV) terminal oxo and imido complexes, Cp*M[N(iPr)C(Me)N(iPr)](NSiMe_3) (M = Mo (3) and W (4)) and Cp*W[N(iPr)C(Me)N(iPr)](O) (M = Mo (5) and W (6)), using trimethylsilylazide and either nitrous oxide or carbon dioxide respectively. Results obtained from preliminary chemical reactivity profiles of 3 - 6 for oxo and imido group transfers involving small molecule substrates, such as CO and CNR, will be reported. Highlights of these studies include demonstration of orthogonal routes for the construction of η^2-isocyanates at a common metal center that includes the solid-state molecular structure of the first known k^2-(O,C)-η^2-CNR complex and a rare example of an early transition metal η^2-CO_2 complex, Cp*W[N(iPr)C(Me)N(iPr)](CO) (η^2-CO_2) (7). Progress made towards the development of oxo and imido group transfer catalysts will be discussed, including an assessment of relative metal-dependent energy barriers.

### 304. Ruthenium catalyzed hydrogenation supported by a novel bipyridyl ligand

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We have developed a novel ruthenium chloride pre-catalyst supported by modified bipyridyl ligand. The novel feature of our bipyridyl ligand was the availability of electron donor groups and hydrogen bonds near the metal center; these groups were proposed to improve catalytic activity. This catalyst was shown to be effective in transfer hydrogenation on a series of ketones in both isopropanol and in aqueous/methanol solutions. Results on the hydrogenation of ketones and imines by our pre-catalyst will be discussed. Determination of whether these donor groups within the bipyridyl ligand affect catalytic activity will also be addressed.

### 305. Determination of iron in vitamin pills by a redox titration and spectrophotometry technique.

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The average human body contains 5 to 6 grams of iron. This iron is found in the hemoglobin. Humans obtain iron from their diet in foods such as meats and green vegetables. Dietary supliments of iron...
can be taken to prevent anemia, a condition caused by lack of iron. Most vitamin tablets contain iron (ferrous) in the form of ferrous fumarate.

306. Study of in situ ligand synthesis in the development of uranyl hybrid materials

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Metal-organic hybrid materials consist of metal centers that are assembled via coordination to organic linker molecules to form one-dimensional chains, two-dimensional sheets or three-dimensional frameworks. Such hybrids are typically synthesized hydrothermally by reacting ligands directly with metal salts. An alternative method which has been gaining interest in recent years, however, is to introduce reactive organic molecules which can undergo transformations in situ to form the ligand observed in the solid state product. This has several benefits, including simplified ligand synthesis, improved crystal growth and access to materials that may be otherwise inaccessible by direct means.

Here we present several modes of in situ ligand synthesis that have been utilized in our research group to form uranyl coordination polymers. We also describe cases of “serendipitous” in situ reactions such as decarboxylation and oxalate formation. The impact on crystal engineering, implications for solution state chemistry and potential tactics to control in situ reactivity is discussed.

307. Comparison of the reactivities of a terminal alkene and an internal alkyne in platinum-catalyzed hydrosilylation reactions

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The rate of hydrosilylation of an alkyne is known to be greater than that of an alkene in solution and on a solid surface such as a Si(100) surface. Furthermore, terminal alkenes are known to react faster than internal alkenes in hydrosilylation reactions. Hydrosilylations of vinyl and alkenyl substituted silicones are integral to numerous industrial applications. In principle, alkenyl silicones can replace alkenyl silicones in such applications and provide an additional degree of reactivity due to their triple bonds. In addition, for synthetic reasons, silicones with internal alkynes are easier to prepare than ones containing terminal alkynes. However, there is no clear trend with regard to the relative rates of addition of a silane (R3SiH) to internal alkynes versus terminal alkenes. Silicon compounds containing both an internal alkyne and a terminal alkene group provide an opportunity to explore such trends. This talk will discuss such studies.

308. Organoaluminum effect on stereoselection in heterocyclic amines

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The effect of organoaluminum on stereoselection in heterocyclic amines is being investigated. The coordination of the organoaluminum and an electronic vs. steric effect on the stereoselection will be discussed. [http://JulietHahn.com](http://JulietHahn.com)

309. Synthesis and characterization of Zn bis β-difunctional complexes for the fabrication of ZnO via metal organic chemical vapor deposition for applications in Microelectronics

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A series of Zn bis β-difunctional complexes were synthesized and evaluated for use as precursors for MOCVD of ZnO thin films. The free ligands were prepared via the reaction of N, N-diethylacetoacetamide and 2, 4-pentanedi one with the appropriate amine. The single source precursors were synthesized via the reaction the free ligands with diethylzinc. The isolated products were characterized using FT-IR, 1H-NMR, 13C-NMR, GC-MS and MALDI. The volatility and thermal stability of the precursors were assessed using TGA. Thin films of ZnO were grown on a SiO\(_2\) substrate utilizing a horizontal hot-walled CVD reactor. The thin films were characterized using SEM and XPS and employed in the fabrication of a transistor.

310. New Au(III), Pt(II) and Pd(II) complexes with water soluble iminophosphorane ligands as potential anticancer drugs

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Platinum drugs are well known and have been widely used for their chemotherapeutic properties in anticancer treatments, although they present serious disadvantages as severe side effects and acquired resistance to the drugs. In the search for new alternatives, not only new ligand sets but transition metals must be explored.\(^{1}\) Our approach\(^{2}\) is the preparation of new iminophosphorane ligands derived from water soluble phosphines, such as 1,3,5-Triaza-7-phosphaadamantane, in an attempt to modulate the hydrophilicity/lipophilicity of the new potential drugs.


311. Luminescent di and trinuclear organometallic gold(I)-M (Au\(_2\), Au\(_2\)Ag and Au\(_2\)Cu) compounds containing bidentate phosphanes as active antimicrobial agents

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We report here on the synthesis of new dinuclear gold(I) organometallic complexes with silver(I) and copper(I) containing mesityl ligands and bridging bidentate phosphanes. The new complexes
lead to the formation of a family of heterometallic clusters. A study of their luminescence properties revealed that all compounds are phosphorescent in solid state at low (77 K) and room temperature. More importantly, compound \([\{\text{Au(m-mes)}_2\text{(m-dppy)}\text{Ag}\}]\text{ClO}_4\) resulted luminescent in dmso solution at room temperature. Previously reported compounds \([\{\text{AuCl}_2\text{(m-LL)}\}]\) (L-L = dppe/dppy) were also studied for comparative purposes. Selective and effective antimicrobial activities against Gram-positive and Gram-negative bacteria and yeast were evaluated for all compounds. They all display moderate to high antibacterial activity while heteronuclear \(\text{Au}_2\text{M}\) derivatives are the most active and were also potent against fungi. The minimum inhibitory concentration ranges from 1 to 10 \(\mu\text{g/mL}\) for silver complexes and are 10 times more active than the silver salts.


3. Titanocene-phosphine derivatives as precursors to cytotoxic heterometallic TiAu$_2$ and TiM (M = Pd, Pt) compounds

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Currently the chemotherapeutic options for the treatment of prostate cancer are very limited. Metallopharmaceuticals offer potential advantages over more common organic drugs. Many of the drugs currently used are related to cisplatin and its derivatives. Many of these drugs are toxic to cancer cells in vitro, although they are often toxic to normal tissue and frequently select for initial and acquired resistance to treatment. In the past few years efforts have been undertaken to supplement platinum-based-drugs. Titanium-based-drugs in particular TiCp$_2$Cl$_2$ revealed the highest preclinical activity amount the transition metal complexes and they seemed to hold high potential for treatment of metastatic renal, metastatic breast and prostate cancers, but the mayor drawback of TiCp$_2$Cl$_2$ was lack of hydrolytic stability at physiological pH. Recent studies have indicated that gold complexes also display high cytotoxicity against solid cancer tumors and even against cisplatin-resistant cancer cell lines by a mode of action different from that of cisplatin (mainly affecting mitochondrial functions). Some of the highly cytotoxic gold(III) derivatives in vitro are also cytotoxic in vivo to prostate cancer cells and xenografts while causing minimal systemic toxicity. We have prepared heterometallic titanocene derivatives containing phosphines with Au(I), Pd(II) and Pt(II) as the second metal in the molecule. Our hypothesis is that the incorporation of two different cytotoxic metals in the same molecule may improve their activity as anti-tumor agents. The coordination of the phosphine fragments to Au, Pd and Pt afford stable heteronuclear Ti-M derivatives and we can follow the cleavage of \(\eta^3\) bond between Ti and Cp rings as well as the trajectory of the part of the molecule with the second cytotoxic metal already incorporated to the target. DFT calculations of the compounds have been performed to assess the most plausible structures. These complexes were highly cytotoxic against HeLa human cervical carcinoma and DU-145 human prostate cancer cell lines. Substitution of the Cl ligands by oxalate ligands will be discussed along with studies of the interactions of the new compounds with biomolecular targets (DNA and transport proteins like Human Serum Albumin).
313. Structural effects of de-alloying the less noble metal from silver-gold thin films

**Daniel A McCurry**

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The less noble metal can be removed by selective dissolution (de-alloying) from bimetallic alloys to create a nanoporous structure. Such structures have many applications in catalysis and sensing due to their high surface area to volume ratio. In a Ag-Au alloy, the silver can be stripped from the alloy at potentials positive than the so-called critical potential, that is strictly dependent upon the amount of gold in the alloy. A higher amount of gold generally resulted in a more positive critical potential, but the substrate on which such an alloy is deposited was also found to affect the surface morphology and the critical potential. De-alloying of Ag-Au thin films with sizes between 10 and 100 nm on gold and glassy carbon substrates was compared to the de-alloying of 10-35 nm silver-gold nanoparticles and bulk Ag-Au alloy samples. The alloy composition in the experiments was determined using EDX and surface area developed was measured using Pb underpotential deposition. The thin films deposited on gold followed almost identical de-alloying behavior with the bulk samples, whereas those deposited on glassy carbon had consistently lower critical potentials by about 100 mV. Substantially different to those samples was the de-alloying behavior of the Ag-Au nanoparticles where the critical potentials were consistently lower by about 300 to 400 mV to the bulk samples. The difference in the alloy stability was attributed mainly to size and structural effects evidenced by SEM/TEM and led to substantial changes of the alloy surface properties.

314. Resilin in the engineering of elastomeric biomaterials

**Linqing Li**

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Resilin, the highly elastomeric protein found in specialized compartments of most arthropods, exhibits superior resilience and excellent high-frequency responsiveness compared with many other structural proteins. Facilitated via biosynthetic strategies, different resilin-like polypeptides derived from the *Drosophila melanogaster* repetitive motifs have been produced and characterized. With the maintenance of natural resilin’s mechanical properties, RLPs have been further extended with the incorporation of biological domains, with aims of generating cell-responsive biomaterials in engineering mechanically active tissues such as cardiac tissues, vocal folds, and blood vessels.

315. Oxidation study of PbSe nanocrystal films fabricated using dicarboxylic acids

**Anthony R Smith**

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Long term stability of lead chalcogenides against oxidation has gained considerable interest in the field of photovoltaics. Here, inherent oxidation suppression by carboxylic acid ligands on PbSe nanocrystal films is studied. Dicarboxylic acid linkers were used to fabricate nanocrystal films ~100nm thick through a layer-by-layer dip coating procedure. The oxalic, malonic, succinic, fumaric, and malic acid linkers used provided fast buildup of layers with nearly complete exchange of the oleic acid capping groups on the as-prepared nanocrystals. A red-shift of the first excitonic absorption band
upon initial film formation was analyzed and attributed to increased electronic interaction between
adjacent nanocrystals, an effect that varies with linker length and conformation. The rate of oxidation
of PbSe nanocrystal films under ambient conditions was followed by tracking the blue-shift of this
peak with time using Fourier-transformed infrared spectroscopy. Results suggest that these same
dicarboxylic acids conferred some long-term protection from oxidation compared to the unmodified
PbSe nanocrystals.

316. Uranyl-4,4′-biphenyldicarboxylates: Synthesis, Structure and Fluorescent Properties
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Exploring the synthesis of uranium-bearing materials builds a greater understanding of the environ-
mental challenges posed by the nuclear fuel cycle. U(VI) is a highly mobile species in aqueous media
and becomes a concern to the surrounding biosphere. We have explored the synthesis of U(VI)-
containing materials using a variety of organic compounds, specifically carboxylic acids. The resulting
U(VI)-bearing materials are rich in diversity and generate a variety of topologies. In this investiga-
tion, we employ the organic linker, 4,4′-biphenyldicarboxylate, and observe its different coordination
modes to the U(VI) metal center. A systematic investigation of pH and time has yielded three unique
uranium-containing coordination polymers: (1) \((\text{UO}_2)(\text{C}_{14}\text{O}_4\text{H}_8)\), (2) \((\text{UO}_2)_2(\text{C}_{14}\text{O}_4\text{H}_8)(\text{H}_2\text{O})\) and (3)
\((\text{UO}_2)_2(\text{C}_{14}\text{O}_4\text{H}_8)(\text{OH})_2\). Square-bipyramidal uranium centers linked by 4,4′-biphenyldicarboxylate to
form 2D sheets are observed in Compound (1). The overall 3D architecture in Compound (2) is gen-
erated by point-sharing pentagonal bipyramids. Compound (3) also exhibits this point-sharing mode
along with unusual uranyl cation-cation interactions. Herein we will discuss the crystallographic and
fluorescent properties of the three compounds.

317. Synthesis, Structure and Properties of Uranyl/Organometallic Coordination Polymers
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The uranyl cation \((\text{UO}_2^{2+})\) has been combined with a multitude of organic ligands to yield a large
variety of hybrid materials. Uranyl compounds containing organometallic ligands (i.e. those ligands
possessing an organometallic portion as well as possible coordination sites for a second metal cation)
however, have not been studied as thoroughly. This second “pre-packaged” metal center has the op-
portunity to influence magnetic properties, catalytic activity, photochemical activity and fluorescence
properties of compounds as seen in transition metal frameworks with organometallic ligands. Due to
the stability of the ligand as well as the carboxylate functionality that can coordinate to the uranyl
cation, Ferrocene terephthalate was selected to begin this study. Two unique uranium organometal-
lic coordination polymers were synthesized with this ligand: (1) \([(\text{UO}_2)(\text{Fe}(\text{C}_8\text{O}_4\text{H}_2)(\text{C}_5\text{H}_5))(\text{PO}_4\text{H}_2)(\text{OH})]\bullet(\text{H}_2\text{O})_2\), and (2)
\([(\text{UO}_2)(\text{Fe}(\text{C}_8\text{O}_4\text{H}_2)(\text{C}_5\text{H}_5))_2]\).

Herein we will discuss the synthesis, structures, and physical properties of these compounds.

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318. Synthesis and characterization of a novel uranyl thiophene coordination polymer

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The rational design of hybrid materials containing n-conjugated species and inorganic building blocks represent a new class of emerging materials that combine desirable physical properties characteristic of both components in a single phase. Specifically, transition metal and lanthanide frameworks containing thiophene carboxylates are of special interest as photoactive materials because of its excellent chemical stability, photoluminescent properties, and electronic properties. However, actinide thiophene frameworks containing the UO$_2^{2+}$ cation have not been studied to date and their photophysical properties thus remain unexplored. We report the first example of a uranyl-thiophene coordination polymer Na$_4$[(UO$_2$)$_4$C$_6$H$_2$O$_2$S$_6$], containing two dimensional interpenetrating sheets. This material is characterized by single X-ray diffraction, powder X-ray diffraction, IR spectroscopy, TGA, solid-state UV-Vis spectroscopy, and fluorescence spectroscopy.

319. Analytical characterization and bioaccumulation of gold nanoparticle primary particles, aggregates, agglomerates, and agglomerated aggregates

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The ability of nanoparticles to form larger superstructures of aggregates and agglomerates has been extensively noted in the literature. The in vivo biological impact of these structures, however, has not been assessed. This knowledge gap is especially critical in the safety assessment of nanoparticles to be used for therapeutic purposes. Here we show a reproducible method to form stabilized primary particles, agglomerates, and aggregates. Each of these structures was characterized using multiple techniques to determine size, shape, morphology, and concentration in water, cell media with fetal bovine serum, and 100% rat serum. Results showed that these structures each contained unique characteristics visible by TEM and UV-Vis spectroscopy, and that these characteristics were not significantly altered by the presence of media or rat serum. When administered to a mouse model, these structures demonstrate significant differences in organ and cellular distribution compared to the primary particle building blocks. In addition, different structures produced different blood serum chemistry data. These findings raise the possibility for different mechanisms of toxicity between the structures. Such a possibility necessitates complete characterization and stability assessment of nanomaterials prior to their in vivo administration.

320. Fabrication and characterization of electrospun semiconductor nanoparticle–polyelectrolyte ultra-fine fiber composites

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Fluorescent composite fibrous assembles of nanoparticle-polyelectrolyte fibers are useful multifunctional materials, utilized in filtration, sensing and tissue engineering applications, with the added benefits of improved mechanical, electrical or structural characteristics over the individual components. Composite fibrous mats were prepared by electrospinning aqueous solutions of 6 wt% poly(acrylic acid) (PAA) loaded with 0.05, 0.10, 0.15 and 0.20%v/v, carboxyl functionalized CdSe/ZnS nanoparticles (SNPs). The resulting composite fibrous mats exhibited uniform fiber morpholo-
gies with increasing fiber diameters with increasing SNP loading. Fluorescence micrographs reveal luminescent fibers with evenly distributed fluorophores in the higher loaded samples. Moreover, laser excited fibers manifest SNP intermittency correlated with small clusters and single SNPs suggesting excellent dispersion in the PAA matrix. Photoluminescence spectroscopy of the fiber mats display a SNP emission peak ($\lambda_{em} = 554$ nm) that is red shifted when compared to the emission peak of the SNP-PAA solution ($\lambda_{em} = 525$ nm) due to SNP-SNP energy transfer as the fluorophores are effectively frozen in position by the solid PAA fiber matrix.

321. Post-processing electrospun chitosan fibers

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Electrospinning is an inexpensive and simple method of producing non-woven fiber mats. Electrostatic forces are employed to produce the mats, which intrinsically have larger specific surface to volume ratio and smaller pores than traditional fibers. Fibrous mats are typically used in a wide variety of industries such as filter media, tissue engineering, and sensors. Chitosan, the $\text{N}$–deacetylated derivative of chitin, is environmentally friendly, non-toxic, biodegradable, and anti-bacterial. However, due to chitosan’s solubility in aqueous acids, it is electrospun using trifluoroacetic acid (TFA).

Modified chitosans, such as carboxymethylchitosan, are currently under investigation as a means of creating designed nanofibrous mats with specific chemistries. However, typically an entirely new set of electrospinning conditions has to be developed for each novel chemistry due to differences in solubility and viscosity. In the present study, we have electrospun chitosan mats and post-processed the fibers. Two different post-processing conditions were employed. One post-production procedure, featuring vapor-phase glutaraldehyde, effectively crosslinks the fiber mats utilizing a Schiff base imine functionality. In another post-processing procedure, the as-spun mats are solution-phase post-processed by chemically functionalizing the mats with cyano, carboxylic acids and thiol groups. While both methods maintained fiber shape and characteristics, there is a definite increase in fiber diameters due to processing. FTIR and SEM have been performed on the pre- and post-processed fiber mats. NMR, tensile testing and investigations into the percent modification are currently underway.

322. Effects of changing reaction parameters on Suzuki polycondensations

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Optimization experiments were performed in order to determine the effects of changing reaction parameters on molecular weights of polyfluorenes synthesized via a Suzuki polycondensation reaction. In particular, this research focused on finding the optimal palladium catalyst system to use in our polymerizations. As was the case in our earlier studies on alternating rigid-flexible diblock copolymers, bis[tri(o-tolyl)phosphine]palladium(0), or PdL$_2$, proved to be the best catalyst for the polyfluorene synthesis, providing samples with molecular weights on the order of $10^5$ g/mol when matched with optimized base and solvent conditions. However, considering the air and light sensitivity of this material, we also screened different substituted tris(dibenzylideneacetone)dipalladium(0) precursors, which can form the active PdL$_2$ catalyst when combined with the phosphine in situ.
323. Adsorption of Carbon Dioxide onto Aluminum doped Ferrihydrite

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Surface adsorption of carbon dioxide (CO₂) on soil minerals plays an important role in the properties of minerals, both in term of reactivity and stability. Limited work has been done on the CO₂ adsorption of mixed Al and Fe (oxy)-hydroxides while CO₂ sorption on their single-component Al and Fe counterparts have been widely studied. X-ray photoelectron spectroscopy (XPS), atomic adsorption, transmission electron microscopy with electron dispersive X-ray spectroscopy, X-ray diffraction, and attenuated total reflectance Fourier transform Infrared Spectroscopy combined with density functional theory calculations were used to investigate the gas-phase adsorption of CO₂ on Al-doped 2-line ferrihydrite. Al-substituted ferrihydrite samples were synthesized under atmospheric conditions (i.e. containing CO₂) as well as controlled CO₂ free conditions. The Al content mixed in solution of ferrihydrite varied between 0 and 100 Al mol%. Above Al substitutions of 10 mol%, the experimental results indicated that the nanoparticles consisted of a mixed phase of ferrihydrite and alumina. ATR-FTIR experiments showed that as the Al mol% increased beyond 10%, the bicarbonate complex, formed by passing CO₂ over the particles, exhibited shifts in its vibrational modes due to adsorption on Al-based phases. The presence of hydrogen bonded water on the surface of ferrihydrite and Al-doped ferrihydrite prevented the formation of bicarbonate complexes. While the bicarbonate complex was only found to be stable under dry-CO₂ reactant conditions, carbonate was present whether the CO₂ was dry or contained atmospheric amounts of water vapor.

324. Trifluoro ethanol and ¹⁹F MAS NMR as a terminal hydroxyl probe for zirconium(IV) hydroxide structures

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In recent years there has been much interest in porous materials for the removal of toxic industrial chemical (TICs) and potential chemical warfare agents/simulants (CWAs). Zirconium (IV) hydroxide has been found to have great potential for removal of both TICs and CWAs. Commercially available zirconium(IV) hydroxide materials vary greatly in their physical properties and in their bridging to terminal hydroxyl group ratio, because of varying synthetic methods. There are many instrumental methods for analyzing metal hydroxides. These methods typically only give us insight into either the structural or chemical properties, but not both. Presented here is a novel technique for determining the relative accessibility and reactivity of terminal hydroxyl sites by reacting with 2,2,2 trifluoro ethanol (TFE) and characterizing using ¹⁹F MAS NMR. We show how factors such as bridging to terminal hydroxyl ratio, surface area, and pore size affect the ability of the zirconium hydroxide to react TFE.
325. Preparation and modeling of CuO nanoparticles formation and growth in flame spray pyrolysis

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Copper oxide (CuO) semiconductor materials are of interest because of their promising use for electronic and optoelectronic devices, and the size of CuO for these applications is highly important. In this work, near spherical CuO nanoparticles with aspect ratio of 1.2-1.3 were made by the flame spray pyrolysis (FSP) method. In FSP, flame temperature, residence time, and precursor concentration can be used to control particle size. As the precursor concentration increased from 0.5% to 35% w/w, primary particle size increased from 7±2 to 20±11 nm in diameter. Two flames are chosen for the flame temperature and residence time study: set A is with high total gas flow rate (13.8 L/min), high measured flame temperature (1748 K) and short residence time (55 ms) and set B is with low total gas flow rate (6.1 L/min), low measured flame temperature (1432 K) and long residence time (660 ms). Larger primary particle size was observed in the low gas flow system (set B) due to the long residence time in high temperature zone. For the dependence of temperature on particle size, particles grew to similar diameter, i.e. ~11 nm, in both flame conditions within the temperature of 80% of melting point of CuO but particle having longer residence time, i.e. in set B, the standard deviation of particle size is 45% larger than particle in set A. CuO particle growth simulations based on collision/sintering theory with sintering by solid state diffusion gave a result of 6.7 and 9.0 nm for set A and set B at the assumption of surface tension is 0.5 J/m\(^2\). Comparisons of modeling and experimental results were reasonable.

326. Metal-oxo cluster containing polymer nanobeads as potential contrast agents for MRI

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Magnetic polymer nanobeads have received increased attention, primarily because of the resulting synergistic properties that were found to be promising in biomedical applications such as imaging and diagnosis. In this work, we present a novel way of incorporating a metal-oxo cluster into a polymer nanobead by the miniemulsion polymerization technique. Our work has focused on the mixed metal oxo cluster, \([\text{Mn}_8\text{Fe}_4\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4]\) or Mn\(_8\)Fe\(_4\). Previous work in our lab has shown that Mn\(_8\)Fe\(_4\) has properties that would make it a potential contrast agent for magnetic resonance imaging (MRI). Relaxivity values obtained from NMR relaxation experiments \((r_1=2.38 \text{ mM}^{-1} \text{ s}^{-1}, r_2 = 26.65 \text{ mM}^{-1} \text{ s}^{-1})\) and preliminary MR images show that Mn\(_8\)Fe\(_4\) acts as a T\(_2\) contrast material. Moreover, initial cell studies on two human prostate cancer cell lines, DU-145 and LNCap, reveal that the cluster has low cytotoxicity and may be potentially used \(\text{in vivo}\). One key advantage of Mn\(_8\)Fe\(_4\) is its ability to undergo ligand exchange reactions, thus providing a mechanism for grafting to a variety of supports. Here, we show that by substituting the acetate groups on Mn\(_8\)Fe\(_4\) with the polymerizable ligand, 4-vinylbenzoate, we were able to homogeneously incorporate the cluster into polystyrene latexes via the miniemulsion polymerization process. In addition, the nanobeads were found to be monodisperse in size \((70.9 \pm 9.4 \text{ nm diameter})\), resulting into uniform physical and chemical properties. The resulting hybrid particles have the potential for surface functionalization, making them a promising tool for biomedicine.
327. Preparation of glycomic microarrays using catanionic surfactant vesicles: Applications in diagnostics

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Formation of glycomic microarrays has been accomplished by deposition of catanionic surfactant vesicles on hydrophobically-modified chitosan (HMc). Deposition of catanionic surfactant vesicles on HMc surface was characterized by incorporating a lissamine rhodamine dye. The vesicles were seen to remain adhered to the HMc surface after washing with buffer solution. Detergent washing studies indicated that vesicles remain intact on this surface. Vesicles that were functionalized with glycoconjugates (glucose, lactose) were deposited on the HMc surface to prepare glycomic microarrays. Lectin binding studies show that the carbohydrates on the vesicle surface remain intact and are available for binding. Concanavalin A (Con A) binding to vesicles functionalized with glucose, and peanut agglutinin (PNA) binding to vesicles functionalized with lactose were studied and observed to be selective to respective binding components. Vesicles incorporated with LOS of Neisseria gonorrhoeae showed specific binding with an antibody specific for the LOS. The application of this methodology to diagnostic reagents will be discussed.

328. Fabrication and characterization of UV-emitting defect-free ZnO nanoparticles

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ZnO nanoparticles with near-band-edge ultraviolet photoluminescence and no emission in the visible range were prepared by chemical synthesis using polyvinyl pyrrolidone (PVP) as the capping molecules. ZnO particles were surface-modified by organic acids in a post-synthesis procedure. Infrared spectroscopy (IR), transmission electron microscopy (TEM), uv-visible and photoluminescence spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and powder x-ray diffraction were employed in characterization, structure determination and optical properties of particles and their surfaces. Our results indicate crystalline particles of ZnO are formed with two-kinds of surface binding of organic acids. No photoluminescence in our samples was observed in the visible region, which implies negligible defect formation in the ZnO nanoparticles. The effects of surface groups and PVP on the size distribution and shape were explored and are presented here.

329. Electrical properties of a rod-shaped virus

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The size and biodegradable nature of nucleic acids and polypeptides make them attractive targets for bio-nanotechnology applications. It has already been shown that the 18 x 300 nanometer Tobacco Mosaic Virus (TMV), which is composed of RNA and protein, can serve as a template for surface-area enhanced electrodes in batteries and fuel cells. Here we show that at high humidity, non-metal coated TMV is conductive. At lower humidity it can be used in conjunction with various lithium salts as a humidity-sensitive supercapacitor. Our initial experiments show that changing the charges on the surface of the virion can affect the capacitance and the redox characteristics of the virus.
330. Functionalized metal oxide surfaces for electrocatalytic applications

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Modified electrodes have applications as sensors that would selectively bind metals in a solution or as a platform for catalysis via known transition metal-based electrocatalysts. By covalently binding the catalyst directly to the electrode surface, the catalytic efficiency should increase and the need for timely and costly recovery of the catalyst from the reaction solution should be eliminated. Metal oxide electrode materials can be modified with phosphonic acids as they are able to react with surface oxygen groups present in the metal oxide layer, creating comprehensive coverage of the surface by the phosphonate compound. Through selection of the ω-functional group of the phosphonic acid, various synthetic pathways are available to functionalize the electrode surface with a desired electrocatalyst. Synthetic routes to, and characterization of, functionalized metal oxide electrodes will be presented.

331. Fabrication and characterization of CdTe nano- and microstructures for photoelectrochemical solar cells application

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CdTe is of interest for thin film photoelectrochemical solar cells because of its bandgap (1.4 – 1.5 eV) well-matched to the solar energy spectrum and its high molar absorptivity absorption coefficient. The general goal of our research is to develop a novel electrochemical route to synthesise CdTe nano- and microstructures. The influence of the cathodic potential applied during the deposition process and the annealing temperature applied to the deposited thin films on the thickness, morphological, structural, compositional and photoelectrical properties of CdTe thin films was studied. The preparation of the semiconducting nano- and microstructures of CdTe was performed in a simple and inexpensive one-step electrodeposition process. The obtained thin films were studied by AFM analysis and showed compact, fine grain structures. The bandgap energy of this semiconductor was calculated with the help of UV-Vis reflection spectra. The photoelectrochemical behaviour of CdTe photoelectrode was measured in contact with an electrolyte consisting of aqueous sodium sulfite as a reducing agent. Similar to other narrow bandgap semiconductors, CdTe thin films show potential susceptibility to photocorrosion in aqueous solutions. The polarization range of the CdTe modified electrode was investigated in order to determine the potential range in which semiconductor exhibits photoelectrochemical stability. The conducted investigation has shown that the measured photoresponse is mostly a function of the cathodic potential value applied during the electrodeposition process and photocurrent can be improved by changing the annealing temperature of the created CdTe films. These attractive types of CdTe nano- and microstructures formed in electrochemical techniques present themselves as promising material for photoelectrochemical solar cells applications.

332. Structures of brominated oligothiophenes and ethylenedioxythiophenes: Combined experimental and theoretical studies

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We report herein our findings on the solid state structures of a series of oligothiophenes and ethylenedioxythiophenes (EDOT) endowed with bromine atoms at various positions in the presence/absence of the strong electron acceptor, tricyanovinyl group (TCV). Five compounds were synthesized, and crystallized. Their single crystal structures were determined by X-ray diffraction. The impact of the presence of bromine atoms on solid state packing as viewed through analysis of intermolecular
interactions is examined with emphasis placed on competing Br...Br, N...S, N...O, Br...N and Br...O non-covalent bonding in various structures. These results are compared with published structures on closely related molecules as well as computational data obtained using density functional theory.

333. **Photo-Induced Oxidation of Arsenite to Arsenate on Ferrihydrite**

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Arsenic (As) is a Group I human carcinogen and over 137 million people in more than 70 countries are affected by a high level of arsenic in drinking water, including the United States. Although, As mainly exist in two redox forms As(III) and As(V), As(III) is believed to be 25-60 times more toxic than As(V). Therefore simple water treatment procedures that are capable of inducing As(III) oxidation and or adsorption are urgently needed. In this context, photochemistry of an aqueous suspension of the iron oxyhydroxide, ferrihydrite, in the presence of As(III) has been investigated in our laboratory using various techniques. Both IR spectroscopy and X-ray absorption spectroscopy results show that the exposure of ferrihydrite to As(III) in the dark leads to an adsorbed As(III)-bearing species, but the exposure of this As(III)-bearing surface to light leads to the conversion of adsorbed As(III) to As(V). Analysis of the solution phase shows that ferrous iron is released into solution during the oxidation of As(III) to As(V). The photochemical reaction, however, shows the characteristics of a self-terminating reaction which is likely due to the passivation of the ferrihydrite surface by the strongly bound As(V) product. Our results suggest that ferrihydrite could be potential candidate material for As removal, due to its dual functions as an oxidant (in presence of light) and sorbent.

334. **Studies of phase formation of \( \text{Zn}_1-x \text{M}_x \text{TiO}_3 \) (M= Mg or Mn, \( x < 0 < 0.5 \)) from various wet chemical methods**

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The hexagonal Ilmenite structure of \( \text{ZnTiO}_3 \) possesses attractive dielectric properties that allow this material to be used in microwave applications such as mobile telephones, satellite communication systems and satellite television receivers. However, this compound is very difficult to synthesize due to its narrow temperature stability range. In this study several wet chemical methods including Sol-Gel, Sonochemical and a solution chemical method with a cationic surfactant, were used to synthesize \( \text{ZnTiO}_3 \) and its related phases \( \text{Zn}_1-x \text{M}_x \text{TiO}_3 \) (M=Mg or Mn, \( 0 < x < 0.5 \)). Systematic high temperature treatments were performed to study their phase stability under various experimental conditions. All samples were analyzed using a Rigaku Powder X-Ray Diffractometer. The effects of different precursors, synthetic approaches as well as chemical doping on the phase formation were also carefully studied and will be included in this presentation.
335. Electrochemical studies and material characterization of the electrodeposited film of CuCo$_3$ heteropolymetallic complex

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Electrochemistry of the tetranuclear Cu$_4$Co heteropolymetallic (HPM) complex ($\mu_4$-O)(denc)$_4$Cu$_3$CoCl$_6$.H$_2$O (denc = N,N-deithylnicotinamide) has been investigated. The complex is electrochemically active at a Pt electrode in dimethyl sulfoxide with 0.20 M tetrabutylammoniumhexafluorophosphate as the supporting electrolyte. The electrochemical results show that the complex is initially exhibit redox reaction with no electrodeposition and/or adsorption, and at higher cathodic potential it forms deposited film on the electrode surface. The electrodeposited films of the complex obtained using potentiostatic hydrodynamic electrodeposition technique at various potentials are continuous and well adhered. Energy dispersive x-ray spectroscopy (EDS) of electrodeposited film of the complex reveals that the deposited films are primarily Cu with trace amount of Co.

336. Synthesis and Characterization of Stereoblock and Stereorandom Polypropylenes

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We successfully synthesized polypropylenes having different degree of stereoregularity using single-site zirconium (Zr) metalloocene catalyst and borate co-catalyst. Controlled-stereoregularity enables us to change their properties from plastomeric to rubbery behaviors. We found the materials properties of polypropylenes depend on the concentration of the activated single-site Zr catalysts, which can be controlled by the concentration of borate catalysts. In this manner, synthesized polypropylenes were characterized by gel permeation chromatography (GPC), 13C nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC). The degree of stereoregularity of polypropylenes was consistently changed with the different level of catalyst activation that we targeted and the polydispersity index of all polypropylenes was maintained 1.2~1.3. The crystallinity of each polypropylene was measured by X-ray diffraction (XRD) and changed as a function of the degree of catalyst activation as well. From the mechanical properties of stereorandom polypropylene thin films, we obtained the ultimate tensile strength, cycle test at 300% elongation, and tensile recovery after break of each sample set. Interestingly, the stereoblock polypropylenes showed higher tensile strength and recovery than those of stereorandom polypropylenes.

337. Fluoro-modified melting gels; new materials for hermetic barriers

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New hermetic barriers are desirable materials for electronic industry. Hermetic seals are an essential part of microelectronics, micro-electromechanical systems (MEMS), displays using organic-light emitting diodes (OLEDs) and electrochemical devices, such as microbatteries. These are an important factor in the increasing of the electronics lifetime. These hermetic seals prevent the penetration of outside contaminants such as humidity and other gases to infiltrate into electronic devices and degrading their performance.
It was proved that hybrid organic-inorganic melting gels can be used for hermetic barrier applications. One of the important properties of the melting gels which make these usable as a hermetic barrier is their high hydrophobicity and their lack of porosity. The main objective is to fabricate the hermetic barrier materials which have low temperature of processability and high hydrophobicity. The influence of the fluoro modified alkoxides on the hydrophobicity of the surfaces of the coatings obtained with the fluoro-organic modified alkoxides were studied. Increasing the hydrophobicity of the melting gel controls the repelling of water and blocks the atmospheric moisture. The hybrid melting gels were synthesized by the sol-gel method using mono-substituted silanes and di-substituted silanes. Organo-alkoxysilanes, such as methyltrimethoxysilanes (MTMS), dimethyldimethoxysilanes (DMDMS) were the precursors used for the synthesis of the melting gels. The melting gels obtained were modified using fluoro-organic modified alkoxides such as (3,3,3-trifluoropropyl)-trimethoxysilane (TFPS). The thermal stability of the fluoro- modified and unmodified melting gels were investigated using the Thermal-Gravimetric analysis (TGA) coupled with the Differential Thermal Analysis (DTA) while their structures was investigated using the FT-IR spectroscopy. The hydrophobicity of the surfaces was assessed by contact angle measurements.

338. Structural properties of oxide system derived from sol-gel synthesized Ni-Al layered double hydroxides

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Layered double hydroxides (LDHs) are very interesting for their industrial applications in the field of heterogeneous catalysis and the purification of water containing organic and inorganic waste anions. Catalytic applications of the LDHs, used mainly as calcined forms, have been reported for several reactions, such as basic catalysis (polymerisation of alkene oxides, aldol condensation), reforming of hydrocarbons, hydrogenation reactions, oxidation reactions and support for Ziegler-Natta catalysts. Owing in part to their anion exchange properties, certain LDHs are useful materials for pollution prevention, waste cleanup and have properties suitable for the in situ remediation of contaminated soils.

A series of Ni-Al LDHs \([\text{Ni}_{1-x}\text{Al}_x(\text{OH})_2](\text{CO}_3)_2\cdot m\text{H}_2\text{O}\) have been synthesised by the sol-gel method. The oxidic forms obtained by calcination of LDHs at 450°C and 900°C, respectively were structurally investigated using X-Ray diffraction, IR and UV-VIS spectroscopy. In addition, temperature programmed reduction (TPR) led to a good identification of the oxidic forms. By performing TPR experiments combined with isothermal reduction, it was concluded that the oxides obtained at the two calcination temperatures contained the same type of oxidic phases identified for oxides derived from coprecipitated LDHs, although the difference consists in the different reducibility of the Ni(II) ions. The reactivity of the systems obtained by heat treatment of the sol-gel Ni-Al LDHs was greater than the reactivity of the oxides obtained in case of coprecipitated samples.

These different structural and textural properties of the sol-gel prepared LDHs and their derived oxides can encourage the development of the sol-gel process in synthesis of LDHs, for their application purposes, in catalysis and maybe, in the environmental processes.
339. One-step synthesis of stable fluorescent porous silica nanoparticles

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Highly fluorescent porous silica nanoparticles were synthesized in a water/oil phase using organic templates method. In this work, we introduce a one-step method to label porous silica nanoparticles (PSN), with long term stability, using polystyrene (PS) as the pore template, cetyltrimethylammonium-umbromide (CTAB) as a micelle template, and an embedding “lipid” dye (Liss Rhod PE: dye LR, and Dansyl PE: dye D). The use of a lipid like dye enables it to function as a surrogate surfactant with the primary surfactant CTAB on the organic and inorganic interface. Also, this approach allows us to independently control both pore and particle size by adjusting template monomer styrene amount and water/oil ratio. All above make it an important work in biological applications.

[figure 1] formation mechanism

[figure 2] fluorescent analysis of dye incorporated PSN

340. Magnetic studies of gadolinium doped europium sulfide nanostructures

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Single source precursor routes to nanomaterials of lanthanide chalcogenides have been investigated; of particular interest are size dependent phenomena in the redox active lanthanides of sulfur and selenium. Results are presented on the effect of electron doping on magnetic properties of europium sulfide.

Synthesis and characterization of nanoparticles and bulk polycrystalline material are shown as well as magnetic studies and effects of oxidation. Nanowires of gadolinium doped europium sulfide have been recently synthesized; the morphology and magnetism will be discussed.
341. Application of helium pycnometry for determining integrity of coatings on porous substrates

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For functional coatings such as those which are used for controlled release or oxidative protection of solid drug dosage units, the physical integrity of the coating is important. Any cracks or holes in the coating may compromise its intended function. A method based on helium pycnometry has been developed which is able to differentiate intact coating from partial or flawed coating on porous substrates. This method was applied to in-process samples and final product from multiple coating processes. The in-process data is useful as a diagnostic or scale-up tool for the process, and results on final product were shown to correspond with oxidative stability of a film-coated tablet. The method is non-destructive, and was shown to be more sensitive in detecting flaws than visual or microscopic inspection.

342. Silicon-based Molecular Electronics in the Post-Hype Era

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The journal Science declared Molecular Electronics the “Breakthrough of the Year” in 2001. The year before, President Clinton touted technology developments in his State of the Union Address stating, “Soon researchers will bring us devices that can translate foreign languages as fast as you can talk; materials 10 times stronger than steel at a fraction of the weight; and—this is unbelievable to me—molecular computers the size of a tear drop with the power of today’s fastest supercomputers.” The hype surrounding molecular electronics was so palatable that it led to data falsification and fraud culminating in the 2002 dismissal of Hendrik Schon from Bell Labs. Some have characterized this event and the aftermath as bringing us from the “peak of inflated expectation” to the “trough of disillusionment” to use the Hype Cycle developed by Gartner Research.(**ACS Nano**, 2011, 5(1), p.1-2)

This leaves molecular electronics in the “slope of enlightenment” phase where discovery is far from over, underlying the importance of continued fundamental metrology. This talk will focus on silicon-based molecular electronics discussing some of the important metrology steps that we have accomplished since 2002 as well as directions of future research.

Formation of nanoelectronic architectures with molecular monolayers bonded to silicon has remained a challenge as molecular density can be smaller than self-assembled monolayers on Au and metalization can cause molecular degradation or electrical shorting. To overcome these limitations, we have developed a fabrication approach that generates high-quality, high-yield molecular junctions chemically bonded to Au and Si. This approach is deemed flip-chip lamination (FCL). We use self assembly of thiol-based bifunctional molecules on ultrasmooth gold films (uSAu) on plastic substrates (PET). The flexible gold substrates are flipped and pressed onto H-terminated silicon to promote the anchoring of the monolayer terminus with the semiconductor substrate and ensuring conformal contact at the monolayer/electrode interface within a nanoimprinting tool. The monolayers on uSAu-PET are characterized prior to formation of the sandwich structure by using infrared spectroscopy, spectroscopic ellipsometry, contact angle measurements, and scanning probe microscopy. We examined the influence of FCL process on chemical and conformational changes at the interfaces and within the monolayers in the Si/molecule/metal molecular junction structure by using polarized-backside incident IR spectroscopy. Two-terminal electrical measurements were performed to understand the nanoelectronic architectures.
343. Toward covalent attachment of proteins to solid surfaces

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Our ongoing research involves the covalent attachment of selected proteins to solid surfaces. Since the attachment will be done by native chemical ligation, involving the reaction between a thioester (on the protein) and a cysteine residue, we must derivatize our solid surfaces with the cysteine residue, either directly or by means of a polyethylene oxide linker of the desired length. Reaction schemes for introducing cysteines to surfaces first were developed on model compounds in solution and then were conducted on the solid surface. The quartz crystal microbalance (QCM) and the Sauerbrey equation were used to determine the number of cysteine residues attached per unit surface area. Observed frequency change of the QCM results indicated 4-6 protected cysteine residues per square nanometer of surface, in good agreement with a monolayer.

344. Temperature dependent excimer and exciplex fluorescence of pyrene-containing molecules as probes to investigate the micro-structural features of poly(alkyl methacrylate)

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The temperature dependence of the steady-state and time-resolved fluorescence properties of two types of pyrenyl fluorophores have been investigated in films of five poly(alkyl methacrylate)s (PAMAs), where the alkyl groups are ethyl, butyl, hexadecyl, isobutyl and cyclohexyl. The structures of the pyrenyl probes are shown below. Their fluorescence is sensitive to their interaction with neighboring chains of the polymer or their ability to form excited state dimers (excimers). The temperature dependence of the static and dynamic fluorescence properties has been analyzed to extract information about polymer chain mobility and guest site locations within the films. Thus, the temperatures of the onsets of chain relaxation processes and how the probes move in the glassy melted phases of the PAMAs have been examined and will be discussed. We thank the National Science Foundation for its financial support of this research.

345. Electrical characterization of highly-conformal carbon films prepared by CVD

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For the development of advanced electronic devices with carbon films in multi-layered structures, we investigated the current-voltage characteristics of carbon films prepared by chemical vapor deposition using the 4-point-probe and van der Pauw measurement techniques. Two carbon film geometries
were studied: 20nm carbon thin films on insulating Si$_3$N$_4$ substrates, and hexagonal array of 60nm carbon-nanotubes with high-aspect-ratio in porous anodic alumina templates. Standard photolithography and dry etching processes were used to pattern the films. The films exhibited linear current-voltage characteristics over a broad range of voltages. The in-plane resistivities of the carbon thin films and the carbon films in porous anodic alumina are 6∙10^{-4}\,\Omega\cdot m and 5∙10^{-4}\,\Omega\cdot m, respectively. The upper limit of the cross-plane resistivity of the carbon nanotube array film is 15∙10^{-3}\,\Omega\cdot m. Chemical and structural characterization indicated the films to be amorphous carbon with mixed sp$^2$ and sp$^3$ bonding. The 20nm carbon films exhibited 70-85% transparency for wavelengths from 300-900nm.

346. Silica nanoparticles as diagnostic tools and drug delivery systems

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Recently, nano-scale silica materials have gained attention as potential drug delivery systems and diagnostic tools. Specifically, a significant amount of work has been devoted to developing mesoporous silica nanoparticle (MSN)-based targeted drug delivery systems and fluorescent silica nanoparticle-based biosensors and biomarkers. The increased popularity of these silica nanoparticle systems is due to their ease of preparation and functionalization, stability, and biocompatibility. Here, we report the development of dye-doped silica nanoparticles that have potential application in diagnostics and can be used as a model for drug delivery systems. Incorporation of dye-functionalized fatty acid derivatives into standard sol-gel preparation of MSN yields fluorescent silica nanoparticles. Dye release from these silica particles is 20 times less than the release observed from dye-doped MSN prepared using wet-impregnation methods. The particles retain their fluorescence even after multi-step surface-functionalization procedures. BCA protein assay analysis indicates that the particles can be functionalized with biologically relevant proteins. These protein-functionalized particles have strong, stable fluorescence that is 5 times brighter than CdSe quantum dots. This methodology can be applied to fatty acid functionalized pro-drugs to produce analogous drug delivery systems.

Polymer Chemistry
Organizer, Presiding: P. Kofinas

347. Interfacing Electrolytes with Electrodes in Li Ion Batteries

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In any electrochemical device, the interface between electrolyte and electrode is always the only "legitimate" location where redox reactions should happen. For Li ion batteries in particular, these interfaces become 3D and independent "interphases" that form upon the sacrificial decomposition of electrolyte components during the initial activation of the device, and thereafter constitute the key component that dictates both kinetics and reversibility of the cell chemistry. Named "solid electrolyte interphase (SEI)" after their electrolyte nature, these interphases remain the least understood components in the Li ion chemistry despite focused research in the past two decades.

Aiming to improve Li ion technology beyond its conventional margins, this group at ARL has been attempting to understand these interphases on fundamental levels. Multi-disciplinary approaches have revealed the chemistry as well as formation mechanism of these elusive components, and thus enabled us to possess the initial capability of tailoring desired interphasial chemistries through designing and synthesizing electrolyte components. Direct fruitions have been obtained in forming
interphases that either allow facile Li⁺-transfer, or tolerant high temperature-operation, or stabilize against high voltage (5.0 V) Li ion chemistries.

This talk will summarize these efforts.

**348. Nanostructured Tobacco mosaic virus templates for superior lithium-ion microbattery electrodes**

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We report a new technology for the fabrication of lithium-ion microbattery electrodes with advanced electrochemical performance. The electrodes are prepared using self-assembly of *Tobacco mosaic virus* (TMV) scaffolds containing cysteine (Cys) residues within the virus coat protein. The Cys-modified TMV molecules demonstrate enhanced binding to the Au-coated surfaces through the thiol groups in the cysteines, resulting in preferentially vertically oriented, ordered virus patterns. Using electroless plating, self-assembled TMV particles are covered with a roughly 20 nm thick layer of Ni which serves as a current collector and enables rigidity of the biological templates in the electrodes. Electrochemically active battery materials (~20-40 nm thick layers) are uniformly coated on top of nickel using Atomic Layer Deposition (ALD). Thus, the presented technology combines biotemplating and nanostructuring approaches leading to an increase of the active surface area of the TMV-templated battery electrodes compared to flat analogues. As a result, the electrochemically active material loading is increased without increasing areal footprint, enabling higher energy density. Moreover, the use of nanostructured materials creates larger electrode/electrolyte interface and reduces ion diffusion paths, improving the power density. Previously, this technology has been successfully employed to fabricate Ni/TiO₂ nanocomposite anodes for Li-ion batteries with increased capacities and rapid kinetics. Recently, we have demonstrated that TMV-templated Ni/V₂O₅ cathodes exhibit superior electrochemical performance compared to flat V₂O₅ electrodes (Figure 1). In coin-cell measurements, with electrodes composed of TMV-templated Ni/V₂O₅ core/shell nanostructures, a high specific capacity, an excellent rate capability and cycling stability are achieved. In summary, this work demonstrates that TMV-templated Li-ion battery electrodes show superior electrochemical performance which is attributed to the three-dimensional (3D) nanostructured morphology achieved using the biofabrication technology presented here. Combining this technology with 3D microfabrication methods can create new opportunities in the development of high-performance energy-storage microdevices.
Figure 1. Schematic representation (a, b), morphology (c, d) and electrochemical performance (e-h) of the flat (a, c, e, g) and TMV-templated (b, d, f, h) V₂O₅ electrodes. Inset in b shows TEM image of the single viral nanowire. Cyclic voltammograms (e, f) of the V₂O₅/Li cell were recorded in a voltage window of 2.8-4.0 V with a sweep rate of 0.5 mV/sec. Discharge/charge curves (g, h) were obtained in the voltage range of 2.6-4.0 V at a current density of 2 μA/cm². The data (e-h) are shown for the second cycle.

349. Study of high temperature power and capacity fade of Li-ion batteries with LTO anode

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Lithium titanium oxide, Li₄Ti₅O₁₂ (LTO), has zero strain property for lithium ion insertion/extraction. Its 1.56V vs. Li potential makes it a possible anode material for lithium ion battery. Although the relatively high redox potential of LTO vs. Li reduces the cell potential to below 3 V, if coupled with cathode materials such as LiCoO₂ or LiMn₂O₄, the LTO cells do exhibit some advantage points over the traditional cells made with graphite/carbon anode. LTO cells not only have very long cycle life at room temperature or below, they also have very high rate capability for charge and discharge. Unlike graphitic anode, lithium plating does not form on LTO anode. These characteristics make LTO a good candidate for applications that require high rate, long cycle life and safety. However, recent studies have shown that at higher temperatures above room temperature, the LTO cells exhibit large reduction of rate capability as well as some capacity fade. One possible explanation is that LTO does not form a proper solid-electrolyte interface (SEI) layer, which subsequently prohibits further redox of electrolyte. Without this stable SEI layer, electrolyte decomposition continues with cell operation and this decomposition accelerates at higher temperature. In this presentation, results of cell performance tests at various temperatures are presented, as well as data of preliminary efforts in reducing the loss of power capability at high temperature.

350. Tin/carbon composite anodes for long cycle life lithium-ion batteries

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Lithium-ion batteries have been recognized as an enabling technology for renewable energy storage and an energy source for mobile electronic devices and hybrid electric vehicles (HEVs)/electric vehicles (EVs). In current technology, graphite has been employed as a standard electrode material due to its excellent reversibility. However, one of the key limitations of graphite-based Li-ion batteries is the low lithiation capacity (372 mAh/g) of the graphite anode. To meet the increasing demand of large energy storage and consumption, new materials and technology are required. Sn has received great attention as an anode material with a theoretical capacity of 990 mAh/g, which is much higher than that of graphite. In use of Sn-based anodes, however, the extreme volume change during lithium insertion and extraction will lead to severe particle pulverization and binder breakage, resulting rapid capacity fading. Recent results shown that the introduction of carbon into Sn-based anodes can accommodate the volume change and significantly improve the cycling stability.

Here we report a new Sn/C composite anode with microsphere structure. The composite was prepared by hydrothermal method from a suspension/solution precursor. High capacity, excellent cycling stability and rate capability were demonstrated. The initial capacity is 534 mAh/g at the current density of 500 mA/g. No capacity degradation was observed even after 600 cycles, which is much better than those previous reports. The capacity of over 800 mAh/g at a lower current density of 50 mA/g was achieved, higher than most reported Sn/C composites. The high performance is believed to result from the facts that the carbon in the composite sphere effectively accommodates the huge volume expansion/contraction and releases the stress during lithium insertion/extraction.
351. Water-to-O$_2^-$ binding motifs of O$_2^-(H_2O)$ and their controlling factors

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The potential energy surface (PES) of O$_2^-(H_2O)$ is investigated by varying the inter-oxygen distance of O$_2^-$ via ab initio calculations with a large basis set. Although two stationary points, C$_s$ and C$_{2v}$ conformers, are found along the inter-oxygen-distance coordinate, only the C$_s$ conformer is identified as a minimum-energy species. We find a critical distance, $r_c$, separating these two conformers in the PES. The C$_s$ conformer prevails at inter-oxygen distances of O$_2^-$ that are less than $r_c$, while the C$_{2v}$ conformer dominates at the distances larger than $r_c$. The structural features of these two conformers are also discussed. Although the water deformation energy is shown to be the stabilization source responsible for the prevalence of the C$_s$ cluster conformer at the inter-oxygen distances of O$_2^-$ less than $r_c$, the ionic hydrogen bonding is the major driving force for transformation of the water binding motif from C$_s$ to C$_{2v}$ when the inter-oxygen distance of O$_2^-$ increases.

352. Effects of SDS, CTAB, Triton X-100 and the binary mixtures of Triton X-100/SDS and Triton X-100/CTAB on the electron transfer reaction between tris-2, 2’-bipyridyl iron(II) and azidopentacyanocobaltate(III) complexes

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Electron transfer reaction between [Fe(bpy)$_3$]$^{2+}$ and [Co(CN)$_5$N$_3$]$^{3-}$ has been studied in SDS, CTAB and Triton X-100 surfactants media at 35°C and in the presence of 0.1M NaCl. Both SDS and CTAB inhibit the reaction while Triton X-100 showed little or no significant catalysis. CTAB was found to inhibit the reduction of [Fe(bpy)$_3$]$^{2+}$ by a factor of 2.79 at pre-micellar concentrations of CTAB. In SDS, inhibition factors obtained were 1.94 and 2.53 at pre-micellar and post-micellar concentrations of SDS respectively. The binding parameters for the observed inhibition were obtained using Piszskiewicz model for which cooperativity index $n$, is greater than 1 in all cases. Fairly constant $\Delta G^\circ$ values suggests similar mechanism for the electron transfer processes in micellar free and micellar medium. Binary mixtures of Triton X-100/SDS and Triton X-100/CTAB exhibit stronger inhibition of the reaction at premicellar concentrations of Triton X-100 but shows rate enhancement above the CMC of Triton X-100. The results are explained in terms of strong interactions between the surfactants in the mixtures.

353. Coherent anti-Stoke Raman scattering (CARS) microscopy of central nervous system (CNS)

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Coherent anti-Stokes Raman scattering (CARS) microscopy is ideally suited to study structural changes in the myelinated axons found in the white matter of neural tissues, as the CARS microscopy technique is highly sensitive to the Raman mode of aliphatic C-H symmetric stretching vibrations that
arise from the lipids in the myelin sheath. The technique allows for high-contrast, label-free imaging of the myelinated axons. In this study, we demonstrate the feasibility of the CARS technique for imaging post-mortem neural tissue fixed in formalin, including cerebrum, spinal cord, corpus callosum, cerebellum, medulla, and the hippocampus. The CARS images of these features provide neuroanatomical information not observable by histology or magnetic resonance imaging (MRI), which is critical to study cognitive impairment arising, in part, from disruptions in connectivity of the fiber tracts that form the neural network in the central nervous system (CNS).

354. N3-type dyes for open-circuit photovoltage studies

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The dye-sensitized solar cell (DSSC), made of a sensitizer, often a ruthenium dye, anchored to a semiconductor surface such as TiO₂, has shown promise as an alternative source of power. In the DSSC, power is a function of voltage and current, where the maximum voltage available from the cell is the open-circuit voltage. Much work has been done studying efficiency; however, factors affecting open-circuit voltage are not well understood. Some of the most promising dyes for DSSC are the N3-type dyes, which consist of two dipyridyl ligands and two isothiocyanate ligands coordinated to a ruthenium(II) center. Here we have studied novel N3-type dyes modified for distance dependence effects and to investigate factors affecting open-circuit voltage. Rigid oligophenyleneethynylene spacers have been employed to increase the distance of the isophthalic acid anchoring group (which is attached to the TiO₂) to the Ru sensitizer. These dyes have shown excited state injection at high yields with a rapid rate (kₑ > 10⁸ s⁻¹) comparable to N3. Also observed were decreased recombination rates and increased irradiance dependence upon open-circuit photovoltage for an increased spacer length. These dyes have allowed us to probe the relationship between the open-circuit voltage and the diode equation and specifically examine the ideality factor. These modified N3-type dyes show considerable promise for studying DSSC dynamics with decreased charge recombination rates and high open-circuit voltage at higher irradiances.

355. Synthesis and Electrochemical Studies of ruthenium (Ru) complexes containing multiple metal centers

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Transition metal complexes containing multiple metal centers have recently been of interest in light harvesting experiments where exposure to solar energy produces an excited state capable of reducing water to hydrogen. Ligands that facilitate the synthesis of ruthenium (Ru) complexes containing 1, 2, 3, or 4 redox centers, as well as the bi, tri, and tetrametallic complexes that result from these ligands, have been synthesized in good yield and good purity. The redox properties of these molecules have been investigated through cyclic voltammetry; diffusion coefficients have been measured for each complex using both a stationary and a rotating disc working electrode. As expected, the complexes with multiple metal centers have smaller diffusion coefficients (i.e. are larger) than Ru(bpy)₃. Collection experiments utilizing a rotating ring-disc electrode were carried out in order to investigate the efficiency of electron transfers between the working electrode and redox centers at some distance from that electrode. While the value of the collection efficiency is typically invariant and depends only on the geometry of the electrode, the values obtained from these experiments decreased from 24% to 6% as the number of redox centers increased from 1 to 4. These results indicate that electron transfer events in macromolecular species containing multiple redox centers cannot simply be thought of as a collection of electron transfers into isolated redox centers; the morphology of the molecule does matter. Future work will focus on synthesizing the analogous family of iridium (Ir) complexes and on photochemical studies of the light harvesting abilities of these complexes.
356. Application of an electrochemical method that can be used to probe the distal residues in heme proteins to elucidate their roles in oxygen binding and reduction

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Heme proteins perform a wide range of activities from oxygen binding in myoglobin to O-O splitting in heme peroxidases. Spectroscopic studies of heme proteins have shown the importance of distal amino acids in the functions of these proteins. In this study, we used an electrochemical method to measure the interaction between a nearby distal histidine in myoglobin and a heme-bound fluoride ion. Our results show that, in contrast to native myoglobin, the midpoint potential of fluoro-myoglobin is strongly dependent on the pH of the solution in 6.5 to 4.5 region. In this pH interval, the midpoint potential decreases from 0 mV down to a limiting value of -45 mV (vs SHE). The shifts in the midpoint potentials coincide with the pK of the distal histidine at pH= 5.9. The hydrogen bonding energy between the heme-bound fluoride ion and the histidine residue is 4.8 kJ. This is a promising method that can be used to probe the nearby distal residues in heme proteins in their oxidized state.

357. Characterizing the protein environmental effects on the reduction potential

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The protein environment plays a critical role in determining the reduction potential ($E^\circ$) of redox sites in electron-transfer proteins by burying the redox site in a tunable, low-dielectric environment. The two most important environmental factors in determining $E^\circ$ are the degree of burial of the redox site within the protein and the degree of polarization inherent within the fold of the protein, which is further tuned by the sequence. Here, a Dielectric-Electric Spheres (DES) model of redox proteins is developed to determine the environmental contribution to $E^\circ$. The redox site burial is characterized by an effective protein radius, $R_p$, and the degree of polarization is characterized by the average electrostatic potential at the metal atoms, $\Phi$. Both values are determined from continuum electrostatic calculations using crystal structures of the proteins. The DES model demonstrates that $R_p$ and $\Phi$ characterize the outer sphere contribution to the $E^\circ$ with larger $R_p$ leading to lower $E^\circ$, and positive $\Phi$ leading to higher $E^\circ$. Moreover, the DES model works for all redox couples and can be used to predict the relevant couple for a redox site.
Organic monolayers at the surfaces of aqueous aerosols play an important role in determining the mass, heat transfer rate and surface reactivity of atmospheric aerosols. They can potentially contribute to the formation of cloud condensation nuclei (CCN) and are involved in a series of chemical reactions occurring in atmosphere. Recent studies even suggest that organic-coated interfaces could have played some role in prebiotic biochemistry and the origin of life. However, creating reproducible, well-characterized aqueous aerosol particles coated with organic films is an experimental challenge. This opens the opportunity for computer simulations and modeling of these complex structures. In this work, molecular dynamics simulation was used to probe the structure and the interfacial properties of the dicarboxylic acid coated aqueous aerosol. Low molecular weight dicarboxylic acids of various chain lengths and water solubility were chosen to coat a water droplet consisting of 2440 water molecules. For malonic acid coated aerosol, the surface acid molecules dissolved into the water core and formed an ordered structure due to the hydrophobic interactions. The acid and the water are separated inside the aerosol. For other nanoaerosols coated with low solubility acids, phase separation between water and acid molecules was observed on the surface of the particle. To study the water processing of the coated aerosols, the water vapor accommodation factors were calculated.

The presence of oxidants such as molecular oxygen and hydrogen peroxide is intriguing in the study of icy outer solar system bodies due to their possible astrobiological importance. Such oxidants are thought to be present due to the radiolysis of icy planetary bodies by energetic particles. Our understanding of the oxidant composition comes from reflectance spectroscopy of the near surface tied with laboratory experiments that simulate the irradiation processes. Despite nearly over two decades of laboratory research and 15 years since the discovery of molecular oxygen on Ganymede, laboratory experiments still cannot fully replicate the production, trapping and subsequent spectroscopy of astronomical observations. Is it time to consider that processes other than radiolysis of a static ice could influence surface composition?

Given that the astronomical reflectance data is sampling only the very near surface of icy bodies, could previously unrecognized surface chemical reactions reflect the near surface composition. Using novel laboratory experiments as evidence, we propose that re-deposition of water molecules and hydroxyl radicals can create oxidant-rich ices that behave differently than irradiated ices, that may help to explain the production and trapping of molecular oxygen. This paradigm shift may have important consequences in how we use laboratory data to interpret astronomical data.
360. Isotope Effects in Inelastic Collisions of Vibrationally Excited Aromatic Molecules

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Quantum state-resolved energy flow dynamics are investigated for inelastic collisions of highly vibrationally excited molecules with HCl and DCl. Pyrazine molecules are pumped into high vibrational states, with $E_{\text{vib}} = 108$ kcal/mol using pulsed $\lambda = 266$ nm light from a Nd:YAG laser. The outcome of collisions is probed with high resolution transient IR absorption spectroscopy of individual quantum states of HCl or DCl. The nascent energy partitioning of the scattered HCl and DCl molecules is used to quantify the mechanism of the collisional energy transfer. Results show how moments of inertia impact rotational and translational energy gain. The rate of quantum state-specific population change is also known from these measurements.

361. Combined quantum and Poisson Boltzmann method for calculating reduction potentials of blue copper protein analogues

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Accurate and robust calculations of the reduction potentials of the type 1 copper sites in blue copper proteins are necessary due to the vital role these electron transfer proteins play in the biochemistry of many plant and bacterial organisms. The transferability of methods previously developed by Ichiye et al for iron-sulfur proteins is investigated in this work. Here, density functional theory (DFT), at the B3LYP level, is used to calculate structural and energetic properties of analogues of the blue copper redox site. The reduction potential is a function of the free energy of the reduction reaction, which has contributions from the free energy of the copper site and the protein environment. The effects of two basis sets (6-31G** and DZVP2) on the optimized geometry, charges, normal modes, and free energies of the copper site are explored. Diffuse functions on the sulfur atoms were found to be important in iron-sulfur protein calculations, so their inclusion in calculations of the copper site is also considered.

362. Synthesis and characterization of iron oxide nanoparticles

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The formation of iron oxide nanoparticles by thermal decomposition of iron(III) acetylacetonate ($\text{Fe(acac)}_3$) in the presence of organic reducing surfactants is investigated. The composition and surface properties are studied through the use of FT-IR, differential scanning calorimetry, thermogravimetric analysis, and powder x-ray diffraction. Oleylamine was found to be a reliable surfactant, and intermediate concentrations of oleylamine and $\text{Fe(acac)}_3$ produced the highest quality nanoparticles. Alcohol and amine surfactants showed similar affinity when used together, but organic acids resulted in no particle formation when used in high concentration. Higher reaction temperatures lead to larger particles. UV-vis spectra have shown that during synthesis, amine surfactants likely form a stabilizing monomer complex through the formation of an iron-nitrogen bond. Particles capped with oleylamine as the only surfactant were calculated to have a surface density of $1.2 \pm 0.5$ molecules per nm$^2$. 
Reactions of methyl radical with hydroxyl radical are of great combustion importance. In this work three reactions were experimentally studied:

\[ \text{OH} + \text{CH}_3 \rightarrow \text{H}_2\text{O} + \text{CH}_2 \]  

\[ \text{OH} + \text{CH}_3 \rightarrow \text{CH}_3\text{OH} \]  

\[ \text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6 \]  

\[ \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O} \]  

\[ \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2 \]

Previously, reaction 1 was studied only at relatively low pressures. In this work, reactions 1 - 3 were studied over extended pressures (1 - 100 bar for reaction 1 and 2 and 0.01 - 100 bar for reaction 3) and temperature (295 - 714 K) ranges. Hydroxyl radicals were generated in reaction of excited oxygen atoms O(\(^{1}\)D) with water molecules:

\[ \text{H}_2\text{O}/\text{Ar} \text{ lamp and xenon arc discharge lamp were used to monitor the hydroxyl and methyl radicals at ca. 308 nm and 216.4 nm, respectively. Helium was used as a carrier gas. Acetone in water mixture introduced in the system by syringe pump.} \]

The rate constant of reaction 1 is independent of pressure as depicted in (Figure 1). However, there is a negative dependence of the rate constant on temperature. The absolute value of the rate constant is about factor of two higher than that reported by M. Pilling with coworkers and in agreement with the recent high temperature shock tube kinetic studies by Krasnoperov and Michael (2002) and Hanson et al. (2007) (Figure 2).

Rate constant for reaction 2 was also found to be independent of pressure and possess the negative dependence on temperature. However, rate constant of reaction 3 was measured from 0.01 bar to 100 bar and temperature 295K-714K. The rate constant of reaction 3 decreases with the pressure. The rate constant of reaction 3 varies from \(2.6\pm0.2\times10^{-12} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}\) (0.01 bar) to \(1.8\pm0.25\times10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}\) (100 bar). It also has negative dependence on temperature.
364. Reaction of methylenehydrazine with singlet oxygen (\(^{1}\text{O}_2\))

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Based on DFT \([\omega\text{B97X-D/6-311+G(d,p)}]\), and G4 and CBS-QB3 calculations, we examine possible mechanisms for the reaction of methylenehydrazine with singlet oxygen. Calculations were done in the gas phase and with CPCM in water and acetonitrile.

365. Investigation on sensitized chemiluminescence systems and their mechanism for coumarin based on \(\text{H}_2\text{O}_2\)-Fenton Reagent and \(\text{Na}_2\text{SO}_3\)-\(\text{KMnO}_4\), respectively in aqueous medium

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Chemiluminescence emission analysis has the advantages of high sensitivity, wide dynamic range and relatively simple and inexpensive instrumentation\(^1\), and has been frequently used for analysis of pharmaceuticals in recent years\(^2\).

The aim of this work is to use a known simple and rapid method for the determination of naproxen (NAP) and coumarin that does not require sophisticated instruments but give results comparable to those obtained by existing optical methods. The optical properties of NAP were studied in the presence of hydrogen peroxide (\(\text{H}_2\text{O}_2\)) and Fenton Reagent. The optical properties of coumarin were studied in the presence of \(\text{Na}_2\text{SO}_3\) and \(\text{KMnO}_4\). Results will be presented for both systems.

References:
366. Torsion potential for hydroxylamine

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An ab initio potential for the torsional motion in hydroxylamine will be presented. The potential energy surface was calculated at the CCSD(T) level using the cc-PVTZ basis set. The effect that other coordinates have on the torsional motion has been calculated along with the various equilibrium structures.

367. Quantum calculations on (H2O)x.HO complexes

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The OH radical is an important species in physical and biological processes occurring in all aqueous environments. It is known to form stable complexes with water and other species. In the past, several workers have studied the infrared spectroscopy of this radical in rare gases matrixes. Three absorption bands (at 3452.2, 3442.1 and 3428.1 cm⁻¹) were identified and assigned to the OH radical stretching mode in the H₂O.HO complex (2A²), red-shifted from the free OH radical stretch at 3549 cm⁻¹. The origin of the three bands was attributed to matrix site effects, but it is also possible that very similar species could be the origin of at least one of these bands. Candidates include H₂O.HO (2A¢) and (H₂O)₂.HO. In order to solve this problem, we have explored the geometries of these complexes at the QCISD/6-311++G(2d,2p) level of theory and calculated harmonic vibrational frequencies. The vibrational frequency of the OH radical stretch in these complexes are then refined to an anharmonic frequency by fitting the PES data to a Morse potential, and using a HCAO local mode model.

368. Quantization of the Gibbs free energy levels of enzymes in living cells: Experimental evidence

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The Plank radiation law which successfully explained the blackbody radiation data in 1900 is of the form

\[ y = \frac{(ax^5)}{(e^{bx} - 1)} \] .......................... \( (1) \)

where a and b are constants. Eq. (1) can be ‘generalized’ by replacing x with (Ax + B) where A and B are constants:

\[ y = \frac{a(Ax + B)^5}{(e^{b(Ax + B)} - 1)} \] .......................... \( (2) \)

Eq. (2) has been found to fit not only the single-molecule enzymological data of cholesterol oxidase [1, 2] but also the whole-cell transcriptomics (i.e., RNA) data measured with microarrays in yeast undergoing glucose-galctose shift [2, 3] and protein stability data [2]. These observations suggest that Eq. (2) can be viewed as a universal law governing the thermal transitions/excitations (or Brownian motions) that are essential for blackbody radiation, single-molecule enzyme catalysis, protein unfolding, and whole-cell metabolic regulation.
Garcia-Martinez et al. [4,5], using DNA microarrays, measured RNA levels (i.e., transcript levels, or TL) in budding yeast at 0, 5, 120, 360, 450 and 850 minutes after switching glucose to galactose. We investigated the time course of TLs of about 300 RNA molecules belonging to 15 metabolic pathways. These trajectories can be mapped onto a cluster of points in the 6-dimensional RNA concentration space wherein each point represents an RNA trajectory. The similarity between any pair of RNA trajectories can be calculated as the Euclidean distance between two points in this space.

We find that most (70-90%) of the Euclidean distances between all possible RNA pairs belonging to a given metabolic pathway obey Eq. (2), indicating that the Gibbs free energy levels of enzymes in cells are quantized, just as the fitting of the blackbody radiation data into Eq. (2) implied the quantization of the electronic energy levels in atoms.

An indirect support for the quantization of Gibbs free energy levels of enzymes in living cells is provided by the observations (i) that the complex kinetic patterns of RNA levels in budding yeast undergoing glucose-galactose shift can be expressed as a combinations of the 9 basic modes of coupling between transcriptosomes and degradosome, the two enzyme systems catalyzing the production and degradation of RNA, respectively and (ii) that these modes of coupling can be derived logically based on the assumption that transcriptosomes and degradosomes can each exist in 5 distinct Gibbs free energy levels under the conditions of glucose-galactose shift.

References:

369. Chiral supramolecular structures for the detection of chemical changes in aqueous environment.

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The design and synthesis of novel chiral supramolecular structures based on cholesteric polymers and low molar mass compounds is described in relation to chemical sensors suitable for the detection of pH changes in aqueous environment, and presence of chiral molecules and pollutants.

The designed chiral polymer system responds to the presence of aforementioned agents by changing color and a number of other easily detectable structural and morphological parameters.
The mechanisms of response to different environmental agents and selectivity of the system are discussed in detail and possible applications of chiral detectors are considered.

370. Dependence of Langmuir monolayer lateral compression modulus on molecular length, shape and compression speed

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The lateral compression modulus of Langmuir monolayers of fatty acids with various molecular lengths and shapes were measured as a function of compression speed, in order to study the effect of the molecular structure on the dynamic mechanical properties of the monolayers.

Langmuir monolayers are single layer two-dimensional arrays of organic surfactant molecules at liquid interfaces, most commonly at air-water interfaces. In addition to their importance in the fundamental science of studying the low-dimensional system properties, Langmuir monolayers are of interest to nanotechnology for fabricating chemical and biological sensors, and to biomedical sciences as model systems for studying the properties of cell membranes.

Specifically, at the air-water interface we measured the surface pressure vs. surface area isotherms of the Langmuir monolayers of straight chain saturated fatty acids with 16-carbon atoms, 18-carbon atoms, 20-carbon atoms and 24-carbon atoms lengths [H(CH₂)₁₅COOH, H(CH₂)₁₇COOH, H(CH₂)₁₉COOH and H(CH₂)₂₃COOH, referred to as C₁₆, C₁₈, C₂₀ and C₂₄ acids, respectively] as a function of compression speed. On each isotherm the maximum lateral compression modulus (the measure of the monolayer’s maximum resistance to lateral compression) was determined. We observed a general trend that greater the lateral compression speed, lower the maximum compression modulus, lower the resistance to lateral compression. For the observed trend we propose a mechanism that at high compression speed unevenly distributed local high stress in the monolayer has less time to relax, which leads to earlier local failure of the monolayer at these high stress positions before all the molecules in the monolayer could reach the most compact packing equilibrium state which could display the greatest compression modulus allowed by the material. We observed that monolayers of the straight chain saturated C₁₈, C₁₆, C₂₀ and C₂₄ acids all have their maximum compression modulus at about 19 Å²/molecule, independent of compression speed.

We observed a trend that the monolayers of shorter fatty acid molecules (C₁₆ and C₁₈ acids) on average tend to have higher maximum compression modulus (greater resistance to lateral compression) than the monolayers of longer molecules (C₂₀ and C₂₄ acids) do. We conjecture that the longer C₂₄ and C₂₀ acid molecules are more flexible and have more gauche conformation defects which result a weaker mechanical strength for their monolayers.

To investigate the effect of molecular shape on the monolayer mechanical properties, we measured the compression modulus of monolayers of a L-shaped unsaturated fatty acid [cis-H(CH₂)₆CH=CH(CH₂)₉COOH, referred to as cis-C₁₈ acid] and will also measure the monolayer compression modulus of a straight rigid chain trans fatty acid [trans-H(CH₂)₁₀CH=CH(CH₂)₉COOH, referred to as trans-C₁₈ acid]. Preliminary results show that the monolayer of L-shaped cis-C₁₈ acid reaches its maximum resistance to lateral compression at 32 Å²/molecule, larger than the 19 Å²/molecule where the straight chain saturated C₁₈ acid monolayer shows their maximum resistance to compression. The L-shaped cis-C₁₈ acid monolayer has a lower maximum compression modulus than the straight chain C₁₈ acid monolayer does.
371. New method for aerosol measurement of particle density and porosity

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A new application of online tandem differential mobility-particle mass analysis (DMA-APM) for aerosol nanoparticles was developed, which is used to obtain the density distribution directly from the mass and size. It can also detect the reaction evolution, and investigate the mechanism of porous particle formation. Compared with results by the Brunauer-Emmett-Teller (BET) method, this method is more reliable in calculating effective density and porosity. From the tandem DMA-APM method, we found that the density of porous iron oxide increases as the reaction temperature increases, and that particle density shows negative correlation with its size from the same batch. In contrast, for another sample decomposed from copper nitrate, density is not a function of particle size due to its hollow structure and a different formation mechanism.

[figure 1] different structures of particle size effect

[figure 2] densities of particle size and reaction temperature effect
372. Acidic additive effect on immobilized 3,5 dimethylphenylcarbamate of amylose For HPLC chiral separations

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This poster focuses on mobile phase modifier effects on chiral separation of amino acid esters. Acidic additive ethanesulfonic acid (ESA) was studied for the enantioseparation of six pair of amino acid esters with different combinations of standard solvents (hexane/ethanol) and “non-standard” solvents, such as acetone, THF, ethyl acetate, acetonitrile, 1,4-dioxane and methyl t-butyl ether, using Chiralpak IA column, a chemically bonded 3,5-dimethylphenylcarbamate of amylose CSP. Significantly improved selectivity was observed for the enantioseparation of the probe compounds with acidic additive ESA added into mobile phase. The ESA effect was universal under all studied experimental conditions. Van Deemter plot study reveals that ESA inserts its effect by pulling the enantiomer deeper into the chiral cavity of the chiral polymer to increase the interactions between analytes and CSP, which is the main reason for the increased enantioselectivity. Different organic solvent combination study reveals that mobile phase polarity played an important role for the enantioselectivity of the studied compounds. Reversal retention orders were observed with ESA addition and a possible mechanism was discussed.

373. Application of a novel, heated, nine-bounce ATR element and a portable FTIR spectrometer to the rapid determination of total trans fat

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Since trans fat labeling requirements became mandatory in the US and many other countries, there has been an urgent need for rapid and accurate analytical methodologies that would facilitate the verification of compliance with the various regulations. Currently, the minimum level of trans fat and oil in a US product is approximately 1.8% (as percent of total fat); this is the level needed to be measured with confidence to meet the current declaration requirement of zero trans fat, or 0.5 g trans fat per serving, on the US Nutrition Fact label. The determination of total trans fatty acids by infrared spectroscopy has been a widely used procedure that has been recently validated and standardized as AOCS Official Method Cd 14e-09 in 2009. The C-H out-of-plane deformation mid-infrared (IR) band observed at 966 cm⁻¹ is uniquely characteristic of isolated (non-conjugated) double bonds with trans configuration. This
latest attenuated total reflection–Fourier transform infrared spectroscopy (ATR-FTIR) official method entails the measurement of the height of the negative second derivative of the trans absorption band. This method for the rapid (5 min) determination of total trans fat was further optimized in the present study. The performance of a novel, miniature FTIR system equipped with a heated 9-bounce diamond ATR crystal was evaluated. A new, lower limit of quantification was determined to be 0.3%, as percent of total fat. Observed data indicate that this methodology and the 9-bounce, portable ATR-FTIR instrumentation could lead to approximately a 5-fold enhancement in sensitivity relative to single-bounce systems, and would therefore facilitate regulatory compliance verification in the analytical lab and in the field in the US and other countries.

374. Rapid determination of total trans fat and total saturated fat by FT-NIR for regulatory compliance

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Since total saturated fat and total trans fat labeling requirements became mandatory in the US, Canada, and many other countries, there has been an urgent need for both rapid and accurate analytical methodologies that would facilitate the verification of compliance with the various regulations. Capillary gas chromatography (GC) has been the industry standard because it provides detailed information on fatty acid composition. However, GC is complex and time consuming. Consequently, the potential of applying Fourier transform near-infrared spectroscopy (FT-NIR) for the rapid (1 min) determination of these fats and oil constituents has recently been demonstrated to be a viable alternative analytical method. This novel approach entailed the development of FT-NIR models based on accurate GC data and the application of partial least squares analysis to observed FT-NIR spectra. Currently commercially available FT-NIR models permit the rapid and accurate determination of the complete fatty acid composition of fats and oils using observed FT-NIR spectral information. This capability allows the rapid determination of the total saturated fat and trans fat contents of edible fats and oils as well as the rapid verification of the amounts declared on the Nutrition Facts labels of various commercial products.

375. Identification of mycoplasma bacteria: Nanoparticle probes and Mid-IR chemical imaging (IRCI) for DNA microarray detection

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The spatial resolution capability of IRCI in the external reflection mode provided intrinsic image contrast and permitted detection of DNA microarray hybridization on glass slides for the first time. The sensitivity of infrared microspectroscopy has been inadequate for directly measuring DNA test samples present at trace levels in microarrayed spots (each approximately 100-200 µm in diameter) on infrared reflective gold-coated slides. However, this limitation was bypassed in the present study. Detection of microarrayed DNA spots by IRCI was possible on glass slides because a strategy was adopted that entailed the selective formation of a silver layer only on hybridized DNA spots. Silver was the non-infrared-absorbing metal layer that was used as the infrared reflective substrate whose single-beam spectrum was measured relative to that of the silicate glass slide. Silicate glass was the infrared-absorbing reference background material available in large excess. The measurement of silver spots relative to silicate glass generated infrared chemical images with high contrast for
DNA microarrays as well as infrared spectra (consistent with both diffuse and specular \(\text{Reststrahlen}\) band) external reflection modes) that were used to estimate the amount of double stranded DNA in a hybridized spot. The species of the genera \textit{Mycoplasma} and \textit{Acholeplasma} are known to be frequent contaminants of primary and continuous cell lines that seriously interfere with the development and production of cell-derived biological and pharmaceutical products and compromise the safety of final biological products. We are reporting for the first time the application of IRCI to the fluorophore-free detection and identification of mycoplasma species. Cell culture-enhanced PCR and microarray methods in combination with IRCI were demonstrated to be a reliable tool for detection of low concentrations of mycoplasmal agents in biological samples. Established strategies involving formation of biotin-streptavidin adducts and silver augmentation of gold nanoparticles facilitated DNA microarray detection by IRCI. The selective silver enhancement of gold nanoparticles in hybridized microarray spots provides the additional benefit of permitting slides to be archived.

376. Probing Aromatic Peptide Aggregation Using Spectroscopy

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Amyloid fibril formation is involved in such diseases as Alzheimer, Type II diabetes, Creutzfeldt-Jakob disease. Amyloid fibril formation is a complicated process promoted by different factors. One of possible causes of the amyloid fibril formation is pi-stacking of aromatic residues of the amino acids. In our work we study aggregation of very short peptide fragment NFGAILSS which was determined in previous works as one of the units causing the aggregation in Amylin or Islet Amyloid Peptide (IAPP). We study the effect of various substituents on the aromatic ring of phenylalanine, which alter electronic structure of the ring. Aggregation rates were determined by using UV turbidity measurements at 405nm. The result of the experiment showed that substitution on the aromatic ring of phenylalanine has an affect on the rate of aggregation. We also did fluorescence measurements to correlate the turbidity data with changes in the environment of the aromatic ring.

377. Application of Constant Energy Synchronous Luminescence for Determination of Critical Micelle concentration of Selected Surfactants

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Synchronous Luminescence Spectroscopy, either at constant wavelength (CWSLS) or constant energy CESLS) has been used for qualitative and quantitative analysis of compounds in a variety of circumstances. However, in this work the CESLS is used to determine the critical micelle concentration, CMC, of different surfactants. CMC is a very important property of surfactants and micelles and therefore it requires very careful, efficient and rapid method for its determination. Seven surfactants were examined in this work. From the results obtained, this technique is useful for both anionic and cationic surfactants. It is also observed that it can be used for both aromatic and linear alkyl surfactants even though the synchronous luminescence energy for both classes of surfactants are different. The CMC values thus obtained for the surfactants studied agree quite well with the literature values. The simplicity, rapidity and efficacy of this technique in CMC determination make it a very promising technique in the determination of CMC of surfactants and its features will be discussed.
378. Perchlorate SERS analysis using cysteamine-modified silver nanofilms – effects of pH and coexisting ions

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Surface-enhanced Raman scattering (SERS) has recently emerged as a tremendous potential method for chemical and biomolecular sensing. Ag nanofilms deposited on roughened Cu foils (Ag/rCu films) were synthesized followed by modification with cysteamine SAMs to result in a more stable, sensitive and reproducible SERS-active substrates (Cys-Ag/rCu) for perchlorate SERS sensing. Perchlorate concentration down to 5 µg L\(^{-1}\) has been detected for wet samples (no need for drying). The effects of pH and coexisting anions including Cl\(^{-}\), HCO\(_3\)^{−}, NO\(_3\)^{−}, H\(_2\)PO\(_4\)^{−} and SO\(_4\)^{2−} on SERS of aqueous ClO\(_4\)\(^{−}\) have been examined using Cys-Ag/rCu substrates in this work. All the anions tested here decreased the ClO\(_4\)\(^{−}\) SERS intensity due to their competitive binding with –NH\(_3\)^{+} groups of Cys molecules on the substrates. The ClO\(_4\)\(^{−}\) SERS would be quenched when the individual anion concentration is higher than 5000 µM. The selectivity of the Cys-Ag/rCu substrate towards these anions was concluded to be in the following order: ClO\(_4\)\(^{−}\) > SO\(_4\)^{2−} > HCO\(_3\)^{−} > NO\(_3\)^{−} > Cl\(^{-}\) > H\(_2\)PO\(_4\)^{−}. In the solution with multiple anions, the perchlorate SERS was affected simultaneously by all the coexisting anions, and the limit of detection was much higher compared with that obtained in the solutions without these anions. The SERS spectra of the aqueous perchlorate at different concentrations in the presence of these anions were analyzed, and the two kinds of calibration curves were fabricated in the different concentration ranges, demonstrated potential of quantitative detection of aqueous perchlorate.

379. Silver nanostructured multilayer films for arsenate SERS sensing in contaminated groundwater

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Arsenic is a natural element, ubiquitous in the environment, cycling through water, land, air, and living systems. It has been recognized as one of the most toxic contaminants and its effective detection on site has been one of the most challenging issues. In recent years, arsenic detection by surface-enhanced Raman scattering (SERS) has been demonstrated by our group and other researchers. In this presentation, SERS detection of arsenate (As(V)) in both spiked and natural contaminated water samples will be illustrated using silver nanostructured multilayer films as SERS-active substrates. The Ag films were fabricated by a facile electroless deposition process and characterized with SEM and UV-Vis spectra. The nanoparticle size and density have been tuned to obtain maximum SERS sensitivity to arsenate by controlling reactants concentrations, deposition time and reaction temperature. Using optimized substrates, arsenate down to 5µg L\(^{-1}\) (~ 70 nM) could be detected. Standard calibration curves were prepared by plotting peak areas of arsenate SERS band centered at 780 cm\(^{-1}\) against the arsenate concentrations (0-1000µg L\(^{-1}\)) for quantitative analysis. A standard addition method was applied for arsenate measurements in groundwater samples. Experimental results indicated that the SERS method could be used for quantitative analysis of As(V) in groundwater.

380. Speciation analysis and detection of arsenic in contaminated groundwater by surface-enhanced Raman scattering

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Arsenic (As) is one of the most toxic contaminants found in the environment, and long-term exposure to arsenic can cause various cancers and other serious diseases. The main species of arsenic found in
the environment are the inorganic arsenite (As(III)) and arsenate (As(V)). Since the toxicity of arsenic depends on its chemical form (generally, As(III) > As(V)), both analysis of total arsenic concentration and speciation analysis of arsenic are important. Surface-enhanced Raman scattering (SERS) has recently emerged as a promising method for chemical and biomolecular sensing. As an ultrasensitive, fast, simple, and cost-effective method, SERS technique is able to not only identify, detect and screen single and multiple contaminants simultaneously in a small volume of sample, but also accomplish the speciation analysis like distinguish between As(V) and As(III) with no need for any complex preparation and separation of samples. In this presentation, speciation analysis and quantification detection of arsenic in spiked water and contaminated groundwater samples will be demonstrated using SERS technique. The fingerprint characteristics of arsenic SERS provides the base of speciation analysis: the SERS bands of As(III) and As(V) appeared at different positions of 725 and 785 cm⁻¹, respectively. Calibration curves were prepared to evaluate the ability of quantitative detection of the SERS for arsenic. A standard addition method was applied to measure the arsenic amounts in contaminated groundwater samples for both As(III) and As(V). The experimental results indicated that the SERS method could be used for speciation analysis and quantitative detection of arsenic in groundwater samples.

381. Multiplex Detection of Tree Nuts in Food Using Real-time PCR

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Approximately 1.4 million Americans are allergic to tree nuts. The only way to avoid a reaction is by not consuming products that contain tree nuts. Thus, there is a need for analytical methods to assure the accuracy of food labels. Commercially available techniques for the detection of tree nuts are limited to ELISA and PCR. Though ELISA-based methods have been extensively evaluated, little has been done to evaluate the PCR methods. Using spiked samples, a commercial PCR assay for the detection of walnuts displayed limits of detection in rice milk, uncooked oatmeal, cooked oatmeal, and Tris buffer of 45, 220, 550, and 15 mg/kg, respectively. A limitation of these commercial techniques is that they are analyte specific, requiring multiple separate analyses when testing for an unknown or more than one type of tree nut, a costly and time-consuming process. An assay that simultaneously detects multiple tree nuts provides a solution to this problem. Using published primers, a multiplex real-time PCR assay for the simultaneous detection of almond, brazil nut, cashew nut, hazelnut, pistachio, and walnut in food was developed. The Agilent 2100 Bioanalyzer was used to distinguish between the six PCR products. The sequences of the amplicons for almond, hazelnut, and pistachio were identical to the expected sequences. However, the amplicons indicative of the presence of brazil nut, cashew, and walnut were too small for the sequencing method employed. Depending on the tree nut, the assay reliably detected 3-8 mg/kg cooked in oatmeal and 16-38 mg/kg in rice milk.

382. Analytical detection of nitroxyl (HNO) using membrane inlet mass spectrometry (MIMS)

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Nitroxyl (HNO) is the protonated one electron reduced product of nitric oxide (NO). Recent research has shown that HNO has important and unique biological activity especially as a potential alternative to current treatments of cardiac failure, generating increased interest in its chemistry. The spontaneous dimerization of HNO makes it difficult to study experimentally. Indeed, a viable method for its direct detection in solution or biologically relevant preparations is not currently available. A novel way to observe HNO directly involves the study of HNO via membrane inlet mass spectrometry (MIMS). MIMS is a method to sample gases dissolved in liquid phases through the use of a semipermeable membrane that allows the dissolved gases, but not the liquid phase, to enter a mass spectrometer. In recent years
MIMS has been shown to be an efficient, fast, and selective way to detect volatile organic compounds in water and it has also been successfully used to detect nanomolar levels of NO in aqueous solutions and blood samples. We have used MIMS to detect HNO and its dimerization product nitrous oxide (N₂O). Using the MIMS method we have also been able to distinguish HNO from NO by anaerobic quenching of HNO with glutathione. Based on our results, we find that Angeli’s salt (AS), although a well known and respected HNO donor is not completely ideal because it produces a small amount of NO under physiological conditions. We also report MIMS experiments with a new HNO donor, 2-bromo-Piloty’s acid (2BrPA), and compare the usefulness of AS, 2BrPA, and Piloty’s acid (PA) as HNO donors under physiologically relevant conditions. Further work to show the utility of the MIMS method to detect HNO generated via endogenously relevant pathways is underway.

383. Cytrochrome c unfolding in the presence of Cardiolipin bound phospholipid vesicles

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Interactions of proteins and lipids are believed to be the key factor in the determination of the structural and functional characteristics of membrane proteins. The interaction of Cytochrome c with Cardiolipin (CL) bound anionic lipid vesicles disrupts the proteins native structure. The kinetics of this lipid-induced unfolding process were investigated in a series of stopped-flow detected fluorescence measurements additionally the final unfolded state was characterized by absorption, resonance Raman and visible circular Dichroism (CD) spectroscopy. The results show that the native structure of Cytochrome c in the presence of CL is disrupted at a higher rate than when in the presence of the lipid vesicles without CL. This suggests that the CL bound lipid environment dramatically accelerates the structural unfolding process of Cytochrome c. Based on fluorescence data a kinetic mechanism on the vesicle surface is proposed. The first kinetic phase of reflects the conversion of the cyt₂, similar to the native state, to a partially unfolded state cyt₃, which converts into cyt₄ and subsequently in cyt₅. Given that the unfolding process did not fully level off at the end of our recording time allows for additional phases to exist. While it is clear that different of interactions specifically aid in the binding of Cytochrome c to Cardiolipin, a detailed scheme of the resultant induced unfolding of the protein has not yet been derived.

384. Metabolism and residue depletion of albendazole in yellow perch

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The residue depletion profiles of albendazole (ABZ) and its major metabolites: albendazole sulfoxide (ABZSO), albendazole sulfone (ABZSO₂) and albendazole aminosulfone (ABZ-2-Λ₃SO₂) were studied in the muscle tissues of yellow perch. A single oral dose of 10 mg/kg ABZ was given to 42 yellow perch, 6 each at 8, 24, 48, 72, 96, 144, and 216 h post dose times via an intra-gastric tube. The muscle tissues with adhering skin were collected and homogenized with dry ice and subjected
to extraction and cleanup procedures. The final sample extracts were analyzed by high performance liquid chromatography (HPLC) with fluorescence detection. The results indicate that ABZ, ABZSO and ABZSO₂ were detectable by 8 h post dose. The parent ABZ was depleted quickly to 13 µg/kg (ppb) by 24 h. Its pharmacologically active metabolite ABZSO was depleted to 15 ppb by 144 h. The inactive metabolite, ABZSO₂, peaked to 446 ppb at 48 h and was still present to 78 ppb until 216 h post dose. One other inactive metabolite ABZ-2-NH₂SO₂ was detected only in 1 fish each at 72 and 96 h post dose at low concentration ≤ 21 ppb.

This study demonstrates that yellow perch biotransforms ABZ mainly into two of its major metabolites, ABZSO and ABZSO₂. The ABZSO₂ is the most persistent metabolite and could potentially serve as a marker residue for yellow perch.

385. Quantification and Compensation of Non-specific Analyte Aggregation in Electrospray Sampling

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Electrospray (ES) sources are commonly used to introduce non-volatile materials (e.g. nanoparticles, proteins, etc.) to the gas phase for characterization by mass spectrometry or ion mobility. Recent studies in our group using electrospray ion mobility to characterize protein aggregation in solution have raised the question as to whether the electrospray itself induces aggregation and thus corrupts the results. In this paper we develop a statistical model to determine the extent to which the ES process induces the formation of dimers and higher order aggregates. The model is validated through ES- differential mobility experiments using gold nanoparticles and a protein molecule (Rmab). The results show that the extent of droplet induced aggregation is quite severe, and that previously reported cut-off criterion are inadequate. We also use the model to discuss the results from an ES-MS (without a neutralizer) study and give an alternative explanation of a data plot in that study. The model is extendable to any ES source-analytical system and to higher aggregation states.

386. Gas-phase chemiluminescence of arsine for the measurement of arsenic in water: Development of a routine analytical technique

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A simple gas-phase chemiluminescence (GPCL) technique based on the reaction between arsine and ozone has been developed for routine measurement of inorganic arsenic in water samples. The excess hydrogen pressure generated in the cell by the reduction of arsenic species in water with NaBH₄ is used to reproducibly transfer arsine into the chemiluminescence (CL) reaction cell to react with ozone. The CL signal is detected by a sensitive photomultiplier tube (PMT), amplified with a series of OPAM gains and recorded with a complete signal processing software. This in-house built instrument is optimized for performance and cost, so that it will be usable under minimum lab infrastructure elsewhere. The technique is calibrated from 0 - 300 µg/L of total inorganic arsenic with a limit of detection (LOD) of 0.4 µg/L and a sample throughput of 20 samples per hour without sampling automation. The technique is validated by Hydride Generation Atomic Absorption Spectroscopy (HGAAS), Hydride Generation Atomic Fluorescence (HGAFS), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPAES), Anodic Stripping Voltametry (ASV) and arsenic kit using certified standards and groundwater samples. The response of the instrument has been studied for a better understanding of the analytical process.
**387. SERS and DFT Study on Antitumor Active Derivative of 1, 4-naphthoquinone**

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2, 3-dichloro-5, 8-dimethoxy-1, 4-naphthoquinone (DDNQ), a derivative of 1, 4-naphthoquinone, has shown anti-tumor, anti-platelet, anti-inflammatory and anti-allergic activities in in-vitro studies. In this report, surface-enhanced Raman scattering (SERS) spectra of DDNQ are obtained on gold and silver nanosphere surface and compared with those obtained in an electrochemical cell. Potential dependent surface-enhanced Raman spectroscopy provided vibrational information on the DDNQ reductive intermediates. Density Functional Theory calculations and potential energy dependence calculations were used for the assignment of the bands in the Raman spectrum to the fundamental modes of the molecule and to interpret the SERS data.


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A long-standing question in evolutionary biology is the origin of hybrid sterility. A useful approach to identify genes that may be involved in hybrid male sterility is to conduct quantitative proteomic analyses of testis from fertile parental species males and sterile hybrid males. In this study, we developed a method to use tandem mass tag (TMT) combined with LCMSMS analyses to compare testis proteomes of Drosophila.

**Methods:** Proteins were extracted from approximately 45 testes of 7-day old Drosophila. Protein concentration was measured by NanoDrop spectrophotometer. Proteins were reduced, alkylated before being digested with trypsin. two 50 µg allocate of tryptic digest were labeled with the two TMT duplex reagents before being combined and fractionated. Each fraction was then analyzed by nanoLC MSMS with LTQ Orbitrap XL. Data dependent MSMS spectra of the 3 most abundant multiply charged ions were acquired with HCD in the orbitrap and CID in the ion trap. The raw data file was processed with Proteome Discoverer, where HCD and CID MSMS spectra of the same parent ion were grouped before being searched with Sequest and mascot search engine against the D. pseudoobscura protein database.

**Result:** For validation of our work flow, we evaluated efficiency of peptide fractionation using Agilent 3100 OFFGEL fractionators. A standard BSA digest was spiked into the two samples with a ratio of 5:1 before labeling. Data was searched against Drosophila pseudoobscura protein database downloaded from www.flybase.org, with the sequence of BSA inserted into the FASTA file. From the ~20 micrograms sample loaded, 438 proteins were identified, of which 227 were identified with high confidence (P<0.05 with more than two unique peptides). Of the 227 proteins identified, 127 were successfully quantified, showing ratios in the two samples (127/126) 0.8~1.0 for Drosophila pseudoobscura proteins and 0.2 for the standard BSA spiked in the sample. A total of 5529 peptides were identified, 80.8% of these peptides were identified in only 1 of the 24 fractions, another 10.7% were identified in 2 fractions, which bring the total of peptides identified in 1 or 2 fractions to 91.5%. Peptides were evenly distributed in fractions 4-18. Fractions at extreme pH (<4 or >8) contained less peptides, which was expected. This work verified that peptide isoelectric focusing and fractionation using OFFGEL electrophoresis is efficient, and LCMSMS analysis of TMT labeled peptides provided reliable quantification of protein relative abundance.
389. Detection and Characterization of Perchlorate/Sugar Homemade Explosives (HMEs) by Liquid Chromatography - Tandem Mass Spectrometry (LC-MS/MS).

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Homemade explosives (HMEs) and improvised explosive devices (IEDs) are commonly used in criminal and terrorist attacks throughout the world. Explosive devices are composed of a fuel and an oxidizer, along with other components that improve handling properties and/or increase the heat of combustion. Inorganic salts, peroxides, and fuels are all commonly used in the production of HMEs. One common recipe for HMEs uses potassium perchlorate and sugar. These components can be separated with ion chromatography and liquid chromatography and subsequently detected using conductivity detection and mass spectrometry. For this ongoing effort, ion chromatographs and mass spectra of perchlorate were acquired using a Dionex ICS-3000 ion chromatography system coupled to an Applied Biosystems API 3200 triple quadrupole mass spectrometer. Liquid chromatographs and mass spectra of various sugars are acquired using an Agilent 1100 HPLC system also coupled to the Applied Biosystems API 3200 triple quadrupole mass spectrometer. In this work, we identified and quantitated pre-blast components of HMEs containing perchlorate and sugar in an attempt to assign attribution. Detection limits for various components found in HMEs are presented as determined through MRM analysis.

390. Challenges in the determination of soluble barium in D&C Red Nos. 6 and 7 lakes

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Color additives in food, drugs, cosmetics, and medical devices are regulated by the U.S. Food and Drug Administration (FDA). These dyes and pigments must be pre-approved and listed in the U.S. Code of Federal Regulations (CFR) before they may be used in FDA-regulated products. D&C Red No. 6 (R6, Colour Index (C.I.) No. 15850, CAS No. 5858-81-1) is the disodium salt of 3-hydroxy-4-[(4-methyl-2-sulfophenyl)azo]-2-naphthaleneacarboxylic acid. D&C Red No. 7 (R7, C.I. No. 15850:1, CAS No. 5281-04-9) is the calcium salt of the same dye anion. Lakes are prepared either by extending the water-soluble dye onto a substratum such as barium sulfate (R6 lakes) or by synthesizing the dye in situ during the laking process (R7 lakes). The straight colors and lakes must be batch-certified by FDA to ensure compliance with requirements in 21 CFR 74.1306, 74.1307, and 82.5(b)(3), including a specification for lakes of not more than 0.05 percent soluble barium (as BaCl\(_2\) in dilute HCl). Currently, soluble barium in R6 and R7 lakes is determined using gravimetric analysis. In this method, a sample is mixed with dilute HCl and heated gently. The soluble barium is then filtered off and re-precipitated with H\(_2\)SO\(_4\) as barium sulfate. Initial attempts to apply inductively coupled plasma mass spectrometry (ICP-MS) to this method revealed that barium solubility changes with treatment conditions such as sample weight, temperature, and amount of HCl used. In this poster, results obtained from exploring these parameters will be presented.

391. Removal of uranium from seawater using zero-valent iron

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Uranium exists in seawater complexed with carbonate at a concentration of approximately 1.4 \(\times\) 10\(^{-8}\) mol/L (3.3 ppb), giving a total amount of uranium in the oceans of about 4.6 billion tons. This amount
is nearly one thousand times that in terrestrial uranium ores. If this uranium can be extracted from seawater, it could have many useful applications including its use as an alternative fuel for energy generation. There have been many techniques developed for the removal of uranium, however, they can be costly, complicated, and have low extraction efficiencies when operated on a large scale. This study utilizes zero-valent iron (ZVI) as an alternative for the removal of uranium from seawater. ZVI could potentially be a beneficial alternative because it is low cost, nontoxic, and has been proven as a successful removal agent of organic and inorganic pollutants. This study attempted to remove uranium from aqueous solutions including a bicarbonate buffer (pH = 8) run under anaerobic and aerobic conditions, and coastal seawater. The solutions were passed through columns (flow rate = 0.17 ml/min) containing ZVI alone or a mixture of ZVI and quartz sand. At least 70% of the U was removed in each case. Approximately 60-70% of the U was eluted from the column using 10 ml of 10% nitric acid. This study demonstrates that ZVI is effective at removing U from seawater.

392. **Optimization of microwave accelerated acid digestion of complex mixtures using citric acid for increased throughput**

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Most contemporary high throughput proteomic experiments analyze protein populations by interrogating peptide products of tryptic proteolysis. This lab and others advocate a proteolytic approach using microwave accelerated acid hydrolysis which cleaves proteins on either side of Asp residues. Asp selective cleavage has been shown to generate a more chromatographically diverse peptide set, inherently provide more sequence coverage per peptide, and is known most importantly for its speed and ease of implementation. Here we demonstrate improved results by changing the reagent acid from acetic to citric. Changing this parameter has increased the number of identified hydrophobic peptides/proteins. Presented here are results from a direct comparison of the two acid reagents on the S. cerevisiae ribosome and a plasma membrane enriched fraction from human cancer cells. Also discussed are the bioinformatic challenges to overcome in middle down sized peptide analysis.

393. **Proteomic analysis of MDSC-derived exosomes**

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Exosomes, saucer-shaped vesicles 60-90 nm in size, are formed when multivesicular bodies fuse with the plasma membrane and bud off into the extracellular environment. Current research is focused on characterizing the protein composition of exosomes in order to understand their functional roles in cells. Here, one dimensional gel electrophoresis, followed by in-gel trypsin digestion of 13 slices and subsequent LC-MS/MS analysis (Shimadzu capHPLC coupled to a Thermo LTQ-orbitrap tandem mass spectrometer) of the tryptic peptide mixtures was performed to analyze the protein composition of exosomes shed by myeloid derived suppressor cells isolated from mice. A total of 878 proteins were identified, of which 424 proteins have been previously reported in exosomes isolated from other species.
Trace-level detection of oxygen and moisture in process gases are two main analyses that are typically warranted in determining the quality of ultra-pure specialty gases in cylinders and pipelines. There have been several technologies of detection that have been developed and available for this purpose over the years.

In general, trace oxygen analyses are performed using non-depleting electrochemical analyzers (from vendors such as Delta-F) or paramagnetic analyzers that have high levels of accuracy associated with it. However, there is a high cost related to these techniques, as well. This presentation plans on discussing some of the other techniques including galvanic sensors from different vendors and the analytical aspects associated with these, in comparison to the conventional methods of analyses.

The detection of moisture in trace levels in pure process gases is also very crucial for several processes including semiconductors; however moisture analysis is very challenging since it may be affected by several of the external factors such as temperature, pressure, etc. Several techniques have been traditionally employed for trace moisture analysis such as oscillator quartz crystal, and chilled mirror. Recently, analyzers based on cavity ring-down spectroscopy (CRDS) have been gaining momentum for moisture analysis at ppb-levels for high-accuracy applications in semiconductors and specialty gas markets. However, it is not uncommon to note that majority of the plants world-wide are dependent on the less-accurate, but inexpensive Al2O3-based sensors. A comparison of some of the commercially available capacitance-based moisture sensors will be presented. Some of the important technical aspects such as response time (wet-up and dry-down), stability over time, effect of temperature, and analyses of products at different batches of products will be also discussed, particularly focusing on trace moisture analysis at single digit ppmv levels.

2-hydroxy-1,4-naphthoquinone (Lawsone) is a redox active quinone. In aqueous solutions it shows a pair of quasi-reversible peaks with \( E^{o'} = -0.17 \) V (vs Ag/AgCl); in acetonitrile it shows an irreversible reduction peak with \( E^{o'} = -0.56 \) V (vs Ag/AgCl). Its reduction peak is sensitive to anions such as cyanide, acetate, fluoride and dihydrogen phosphate. Hence the square wave voltammograms (SWV) of \( \mathbf{1} \) are used as electrochemical signals for the detection of the anions. In acetonitrile all four anions quench the reduction peak of \( \mathbf{1} \), with the total quenching happening at 1:1, 1:1, 2:1, and 4:1 anion-to-\( \mathbf{1} \) ratio for cyanide, acetate, fluoride and dihydrogen phosphate, respectively. This is in agreement with results from colorimetric studies. In aqueous solutions, however, the method is highly selective for cyanide (total quenching at 0.3:1 anion-to-\( \mathbf{1} \) ratio), followed by acetate (total quenching at ~ 1:1 anion-to-\( \mathbf{1} \) ratio), while it is essentially non-sensitive to fluoride and dihydrogen phosphate ions. The high selectivity of this receptor toward cyanide and acetate in aqueous media makes it a practical system for monitoring these anion concentrations under physiological conditions.
396. Screening of protein glycosylation in human muscle tissue using lectin enrichment and mass spectrometry

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Protein glycosylation, involving an enzymatic reaction to attach a sugar moiety (glycan) to proteins, is linked to impaired skeletal muscle mitochondrial function. Increases in the post-translational modification of mitochondrial proteins by glycosylation/glycation make them more susceptible to ROS-induced damage and directly impair mitochondrial function. In contrast to the non-enzymatic process of glycation, enzymatic protein glycosylation is site-specific, for example, oxygen (O)–linked attachment of glycans to hydroxyl oxygen of serine (S) and threonine (T) residues, and nitrogen (N)–glycosylation on asparagines (N) with the N-X-T/S motif. Lectins are a group of proteins that have high affinity to carbon hydrates and are used for enrichment of glycoproteins. Peptide N-glycosidase F (PNGase F) specifically cleaves glycan from asparagines in N-linked glycoproteins. Using these two techniques in combination with highly sensitive nanoLC MSMS analysis, we are attempting to determine changes in protein glycosylation following exercise training.

Methods: Human skeleton muscle was obtained from a subject before and after 12 months of exercise training. Proteins were isolated and treated with concanavalin A lectin (conA) columns. The resulting glycoprotein mixture was digested with trypsin. Half of the tryptic digest was submitted for nanoLC MSMS analysis while the other half was further digested with PNGase F before nanoLC MSMS analysis. The resulting data was searched against ipi Human database through Mascot and Proteome Discoverer programs. Search results were combined and filtered using Scaffold Distiller. Scaffold also performed relative protein quantitation by spectral counting.

Results and Discussion: Analysis of ConA lectin enriched proteins resulted in identification of 20 proteins with at least two peptides. In theory, if these proteins contain N-linked glycosylation, we would get better sequence coverage of them in the PNGase digested sample, and those peptides that were only identified after PNGase digestion would have the typical N-X-T/S/C motif for N-linked glycosylation. In β-enolase, we did observe a peptide GNPTVEVDLHTAK only in the PNGase digested samples but not in samples not treated with PNGase, suggesting the N16 in this peptide was glycosylated. The remaining 19 proteins did not show the expected increase in sequence coverage, suggesting that in these proteins, O-linked glycosylation might be the major form of glycosylation. Comparing glycoproteins in muscle samples from the same subject before and after 1 year of exercise training, we can see a trend towards decreased levels of muscle glycoproteins, which is consistent with the decrease observed in the clinical marker of glycosylated hemoglobin.

397. Proteomic study of plasma membrane proteins enriched by cationic nanoparticle pellicles

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Investigation of the plasma membrane proteome in disease-related cells is key to enhancing diagnostic and therapeutic technologies. Currently, lack of achievement has been reported on membrane proteins due to their low expression levels and intrinsic properties. We aim to develop effective methods to enrich plasma membrane proteins and optimize proteomic strategies for hydrophobic protein
identification. The enrichment was performed by adhering positively charged nanoparticles to negatively charged cell surfaces, forming stable and heavy pellicles. We hypothesized that an increase in mass of the nanoparticle pellicles would facilitate better separation of plasma membrane from higher abundant proteins by centrifugation. Various sizes and compositions of nanoparticles, including iron oxide and gold, were evaluated and compared with previously reported silica nanoparticles. Each nanoparticle was characterized by TEM and zeta potential measurement prior to application to human multiple myeloma cells. Protein enrichment efficiency was determined by both Western blotting and high-throughput LC-MS/MS analysis.

398. **Protein modifications of the ribosome in acquired drug resistance**

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Ribosomes play an essential role in converting stored genetic information into proteins. It is the goal of our investigation to determine if ribosomal proteins isolated from a chemotherapeutic resistant cell line evidence changes from the parental drug-susceptible cells that could serve some functional significance to the resistance. We use proteomic tools to determine differences between ribosomal proteins isolated from a cell line selected for acquired resistance to mitoxantrone and from a drug-susceptible MCF7 human cancer cell line.

Ribosomes were harvested from MCF7 cell lines resistant and susceptible to mitoxantrone. Proteins were extracted and precipitated with acetone following Hardy *et al*., 1969 and Barritault *et al*., 1976. For gel electrophoresis, 100µg protein was applied to 18cm 7-11 NL IPG strips. The second dimension was run on large format gels. Two programs were used to compare replicate gel arrays from each cell line. For bottom-up analysis, spots of interest were digested with trypsin using methods from Shevchenko *et al*., 2006. Digests were injected into a Shimadzu nanoLC coupled with an LTQ-Orbitrap. Intact proteins were extracted from the polyacrylamide gels by a modification of the method described by Mirza *et al*., 2000, and their masses determined using the Thermo LTQ-Orbitrap.

\[^{35}S\] Met incorporation measurements at time increments over a 9 hour period demonstrated that ribosomal activity was decreased by about 25% in the drug resistant cell line. Over replicate harvests, no significant differences were found in the number of ribosomes between the two cell lines. However, gel arrays comparing the two ribosomal populations illustrated differences in the protein compositions. The imaging software indicated the presence of new protein spots as well as spots with decreased abundances. Eight spots were recognized to be of particular interest. Three were assigned by bottom-up analysis as variants of ribosomal protein S3, two are variants of the S10 protein, and three recognized as isoforms of L12. Molecular masses and top-down analysis are being used to define the alterations in the ribosomal proteins in conjunction with high coverage bottom up analyses.

399. **Microbial sequestration of carbon dioxide injected in the deep subsurface**

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Carbon capture and storage (CCS) has emerged as an attractive option to offset carbon emissions. However, the effect of injection of supercritical CO₂ in the deep subsurface (1-2 km below the surface) on the structure and metabolic activities of the microbial communities that inhabit the deep geosphere has not been closely examined. Preliminary experiments explored the viability of *Escherichia coli* under these conditions...
coli (E. coli) and Acidithiobacillus ferrooxidans, a model for lithotropic bacteria, exposed to subcritical pressures of CO2 in an ex situ batch reactor. Our results showed that 30-40% of E. coli survived exposure to 65 bar CO2 for 1.5 hours, as determined by plating and colony forming unit counting. Similarly, a significant proportion of A. ferrooxidans cells remained viable after exposure to 52 bar CO2 for 24 hours, as determined by iron oxidation activity. Future studies will focus on characterizing the effects of supercritical CO2 on microbial processes potentially involved in CO2 sequestration, such as biological fixation, carbonate formation, and methanogenesis.

400. CO2 sequestration through mineral carbonation of iron oxyhydroxides
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Mineral trapping carbon dioxide as a carbonate mineral, which is relevant to the focus of our work, is a permanent and secure method of CO2 sequestration. Carbon dioxide sequestration via the use of sulfide reductants of the iron oxyhydroxide polymorphs lepidocrocite, goethite and akaganeite with supercritical CO2 (scCO2) was investigated using in situ attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The exposure of the different iron oxyhydroxides to aqueous sulfide in contact with scCO2 at ~70-100 °C resulted in the partial transformation of the minerals to siderite (FeCO3). The order of mineral reactivity with regard to siderite formation in the scCO2/sulfide environment was goethite < lepidocrocite ≤ akaganeite. Overall, these results demonstrate the potential of carbon sequestration with ferric iron-bearing minerals in the presence of an aqueous reductant. In particular, given the presence of goethite in sedimentary formations, this conversion reaction may have relevance to the underground, geologic storage of carbon dioxide and to the surface sequestration of carbon dioxide.

401. Characterization of viruses, nanoparticles and proteins using Electrospray – Differential Mobility Analyzer
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Here we demonstrate the versatility of Electrospray – Differential Mobility Analysis (ES-DMA), a gas phase electrophoretic mobility technique that can characterize nanoparticles from size 2 nm to 500 nm by the balance of drag and electrical forces. This technique offers multimodal distributions just like Transmission Electron Microscopy (TEM) but only in a few minutes. Its capabilities are demonstrated through different examples. It is shown that ES-DMA can distinguish between partially degraded and intact virus and that it is linear over several orders of magnitude of virus concentration and hence can be used as an assay. This can be of potential importance to the biomanufacturing industry from the perspective of production and quality control of vaccines. Further, it has been used to study protein – nanoparticles, protein-viruses and virus-nanoparticles binding that can further elucidate on nanoparticles – bionanoparticle interactions. Finally, it is shown that ES-DMA can characterize and quantify different oligomers of antibodies thus making it a powerful tool to study antibody aggregation, an important problem in the biopharmaceutical industry.
402. Synthesis and spectroscopic characterization of spiropyran dyes for metal ion detection

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Spiropyrans are a class of photochromic molecules which open when exposed to ultraviolet light and close when exposed to white light. In the open form, the dye is able to complex with metal ions, making it a potentially valuable transducer for a metal sensor. Current work is presented on the synthesis and spectroscopic characterization of two spiropyran dyes with different length carbon chains that terminate in a methacrylate group (see figure). The methacrylate group enables the dyes to be easily incorporated into polymers for application as metal ion sensors, but this work focuses on the spectroscopy of the dye molecules in solution. A six carbon chain dye, 1'-((6-methacryloxyhexyl)-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline] (6C dye) and a ten carbon chain dye, 1'-((10-methacryloxydecyl)-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline] (10C dye) were synthesized and purified by flash chromatography. The structures of both dyes were confirmed through proton and carbon NMR. The photochromic properties of the 6C and 10C dyes were compared to a commercially available spiropyran dye through UV-Visible spectroscopy. The dyes were found to complex with cobalt and zinc ions, similar to the complex seen with the commercial dye. The influence of the dye chain length on the rate of switching from the open to closed form was examined by UV-Visible spectroscopy. Future work will compare the photochromic properties of these dyes in polymer matrixes, and determine their suitability as metal ions sensors.

403. Molecularly imprinted polymers for metal ion detection

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While there are numerous sensors to measure thermal or mechanical changes in our environment, stable sensors available to monitor chemical changes are less readily available. The ultimate goal of this research is to develop a stable and sensitive chemical sensor to detect the presence of metal ions in aqueous environments. To realize this goal, molecularly imprinted polymers (MIPs) have been combined with spiropyran dyes to create polymers that change color in response to metal ions. MIPs are polymers with high selectivity for a particular analyte through chemically specific binding pockets formed during the polymerization process. Spiropyrans are photochromic, meaning that exposure to light changes the color of the dye. Spiropyrans have two states, opened and closed, corresponding to highly colored and colorless states, respectively. Prior to exposure to UV light, the spiropyran remains in a closed state and cannot complex with a metal ion. When it is opened, the dye can combine with metal cations present, which results in a highly colored complex. This binding can then be reversed by exposure to white light, causing the spiropyran to close again and release the metal ion back into solution (See figure).
MIPs designed to be selective for cobalt (II) cations have been synthesized, purified and analyzed spectrophotometrically. Preliminary results have shown an increased response when compared to a control polymer in the presence of cobalt. Due to the specificity of the molecular imprinting process, the response to the presence of a metal ion other than cobalt should be substantially less for the MIP. This has been tested using zinc, and the MIP response to zinc was lower when compared to the cobalt response. Future research will optimize the polymer reagent ratios in an attempt to elicit more dramatic differences in sensitivity and selectivity. Also, variations in the spiropyran structure will be investigated for their impact on the response profiles of the polymers.

**404. Measurement of Trace Arsenic in Groundwater by Reflectance Photometry**

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The formation of $\text{Ag}_x\text{As}_y$ (x=1,2,3 y= 2,1,0) (s) by the reaction of $\text{Ag}^+$ and $\text{AsH}_3$ is the basis for the measurement of trace arsenic with field kits. Millions of groundwater arsenic measurements were done using this technique despite a poor understanding of its analytical chemistry. The accuracy and reproducibility of the kit are often limited by 30-50% rsd. By using a blue LED (470 nm), we have developed a high precision reflectance photometric technique to measure the dynamic color change during the compound formation. This narrow and optimum wavelength allows precise measurement of transient absorbance and the kinetics of the reaction. Using this technique a minimum quantitation limit of 2.0 μg/L (10 x σ<sub>blank</sub>). The detection sensitivity was 1.47 mV.L/μg within a calibration range of 5-100 μg/L ($r^2 = 0.9992$). NIST-SRM and EPA standards (50.0 μg/L) were validated within 3.0 %. The transient reflectance was proved to obey pseudo 2nd order reaction kinetics at all concentrations. The technique developed was tested for its utility by measuring real groundwater samples from USA. Future work is aimed at identifying the color forming compounds- $\text{AgAsH}_2$, $\text{Ag}_2\text{AsH}$, or $\text{Ag}_3\text{As}$ by reflectance IR spectroscopy.

**405. Lawsone as a colorimetric anion sensor**

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2-hydroxy-1, 4-naphthoquinone (Lawsone) 1 is a quinone based chromogenic sensor. It contains naphthoquinone group as a signaling unit. It has been characterized by colorimetric and spectroscopic techniques as anion sensor. This sensor show colorimetric, UV-vis and NMR spectral changes in presence of cyanide, acetate, fluoride and dihydrogen phosphate anions in aqueous acetonitrile as well as in pure acetonitrile. The interaction of 1 with selective anions resulted in dramatic color change from light yellow to orange in acetonitrile. However, in aqueous media, 1 changed color in the presence of CN<sup>-</sup>, OH<sup>-</sup>, and AcO<sup>-</sup> from light yellow to light orange. The resultant Job’s plots indicated a 1:1 stoichiometry for CN<sup>-</sup>, AcO<sup>-</sup> and a 1:2 stoichiometry for F<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> in acetonitrile. The binding constants exhibited 1 as a sensitive and selective sensor for CN<sup>-</sup>; this is due to the strong nucleophilic character of the cyanide anion. The high selectivity of this receptor toward CN<sup>-</sup>, AcO<sup>-</sup>, OH<sup>-</sup> anions in
organo-aqueous media makes it a practical system for monitoring these anion concentrations under physiological conditions.

406. Characterization of polyphenols and associated metabolites using liquid chromatography/mass spectrometry

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Polyphenols are aromatic compounds whose properties are currently being investigated to better understand how they influence human health. There is much research evidence that documents the health benefits of fruits, vegetables, red wine, and green tea. Previous research focused primarily on quantifying the levels of polyphenols found in these foods and beverages, however researchers now believe that polyphenol metabolites also play an important role for maintaining good health. Since polyphenols are metabolized extensively in the body, they are considered the active ingredients in many foods and beverages rather than the precursors. In several recent publications, there has been a growing scientific interest to understand the biochemical mechanisms of how food polyphenolic compounds and their metabolites act as antioxidant, anticancer, and anti-aging agents. The focus of this research project was to use a single quad ESI-LC/MS to characterize a set of polyphenols and their respective metabolites, namely quercetin, naringin, curcumin, catechin, epicatechin, gallic acid, and resveratrol. This work determined the optimal conditions to identify these compounds from a sample, e.g. solvent selection, solvent gradient, and retention times. In addition, the minimum detection limits for these compounds were also established. From our research, curcumin, quercetin, and naringin were detected down to the nanomolar concentrations. In a separate set of experiments, the polyphenol metabolite concentrations were determined using aglycone as an internal standard.

407. Galvanic displacement as a rapid and simple method to fabricate surface enhanced Raman spectroscopy (SERS) substrates

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Surface enhanced Raman spectroscopy (SERS) is an indispensable analytical technique, allowing for ultrasensitive detection of analytes ranging from fluorescent probes to pathogens and environmental contaminants. SERS substrate fabrication can be a time consuming and involved process, especially when advanced processes like electron beam lithography are used to fabricate the substrates. We have developed a rapid and simple method to fabricate SERS substrates using galvanic displacement, a spontaneous electrochemical reaction between a metal ion in solution and a solid metal or semiconductor surface.

This reaction is capable of producing micro- and nanoscale features that generate an enhancement factor of up to nine orders of magnitude under non-resonant conditions. In brief, a solution of silver nitrate is placed on a metal surface and allowed to react for a short time in the dark to avoid photoreduction of the silver ions. The properties of the silver nitrate solution can be altered by adding chemicals such as ammonium hydroxide that can change the free energy of the reaction, affecting crystal growth. Crystal growth is believed to occur at defects in the native surface oxide layer found on metals and semiconductors, and occurs on both highly uniform thin-film surfaces and natural, highly heterogeneous surfaces such as those found on common metal objects.

This method does not require the use of hydrofluoric acid (HF) or other caustic reagents to strip the native surface oxide, unlike many other galvanic displacement reactions. This makes it safer, more
user-friendly, and more broadly applicable in other areas that could benefit from SERS analysis, such as micro total analysis systems (µTAS) and industrial processes. The combination of a rapid, safe, single step, room temperature reaction with the high enhancement factor makes this method of substrate fabrication an ideal candidate for portable SERS sensing, industrial process monitoring, and even undergraduate or high school level instruction in Raman spectroscopy and SERS.

408. New Dansyl-containing fluorogenic calix[4]arene preorganized in the 1,3-Alternate conformation for selective optical sensing of Mercury(II)

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Calixarene derivatives with pendant dansylcarboxamide fluorescent units are promising optical chemosensors of Hg²⁺, with their sensitivity, efficiency and selectivity of metal ion recognition dependent on the macrocycle conformation. To study the effect from the conformational preorganization of the calixarene moiety of such a ligand on Hg²⁺ recognition, a new fluorogenic calix[4]arene fixed in the 1,3-alternate conformation was obtained and its metal ion sensing characteristics studied. In both solvent extraction from aqueous solutions with high content of Na⁺ (C_Na⁺~ 0.1 M; pH 5.0, acetate buffer) and acidic MeCN-H₂O (1:1 v/v) solutions, 1,3-alternate showed selective optical recognition of Hg²⁺ over many alkali, alkaline earth and transition metal cations (e.g., Na⁺, K⁺, Ca²⁺, Sr²⁺, Ba²⁺, Fe³⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺.) Hg²⁺ complexation by 1,3-alternate leads to quenching of the ligand fluorescence intensity via the PET mechanism. The new preorganized fluoroionophore 1,3-alternate demonstrated a more efficient Hg²⁺ sensing than the mobile prototype and two other dansyl-containing analogs fixed in the cone and partial cone conformations.

409. Association of n-Alkylbenzenes with Fulvic Acid in Aqueous Media

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Association of n-Alkylbenzenes with Fulvic Acid in Aqueous Media Mahmud Eljack* and Abul Hussam 1Center for Clean Water and Sustainable Technologies, Department of Chemistry and Biochemistry, George Mason University, Fairfax, VA 22030, USA

Fulvic acid, an omnipresent natural degradation product of plant materials complexes many inorganic and organic chemical species. In this study we have used a custom made high precision head space gas chromatographic technique (HSGC) to study the association equilibria of n-alkylbenzenes (benzene, toluene, ethyl, propyl, and butyl benzene) with fulvic acid in aqueous media at low concentration. A general theoretical model is developed to treat the experimental data that requires no analytical solute standard. The HSGC was able to measure the vapor liquid equilibria at micromolar concentrations n-alkylbenzenes and fulvic acid. This allowed determination of infinite dilution activity coefficients of n-alkylbenzenes in the complex environment. Measured activity coefficients as a function of fulvic acid concentration show that on average 15 benzene molecule associate with one fulvic acid while 5 n-butylbenzene associate with one fulvic acid molecule. The apparent critical association concentration (similar to the crticial micelles concentration for surfactants) fulvic acid was about 3 μM, which is much less than sodium dodecyl sulfate at 8 mM. Preliminary studies showed that fulvic acid has micelle-like properties and could be utilized for applications in understanding bioremediation, and bioavailability of organic compounds.
410. Dynamics of Arsenic Removal by Composite Iron Matrix.

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Groundwater, a primary source of drinking water, in many parts of the world containing toxic level of arsenic and other species is harming the health of millions of people. This study examines small-scale household water filtration systems based on composite iron matrix (CIM) sorbents to obtain potable water. The experiments examine the arsenic removal mechanisms based on surface complexation reactions, sorption dynamics, and kinetics. An equilibrium sorption capacity, \(K_f = 4.25 \text{ mg of As/g of CIM}\), was found within a pH range of 6.5 to 7.5. The sorption capacity appears to increase with time and explained by sorption isotherms calculated from equilibrium surface complexation model. Using this data the filter life span has been estimated to be 14 years to reach the 50 μg/L As (total) breakthrough with 80 L/day influent water containing 300 μg/L As (total). The surface area of CIM was found to be 50 - 70 m\(^2\)/g by a unique headspace gas chromatographic technique. The surface area suggests a Goethite like phase as the active component with 26% sorption capacity. The adsorption kinetics, however, show a fast pseudo-second order rate constants, \(k = 1.07 \text{ and 3.74 g/(mg.min)}^{-1}\) at 1.0 and 10.0 mg/L of As (III), respectively. Small column experiments with size fractionated samples, such as 65 micron CIM particles, showed equilibrium sorption capacity greater than 10.0 mg/g CIM with maximum influent As(III) 10,000 μg/L and the maximum effluent As(III) 23 μg/L. More than 250,000 SONO CIM based filters in Bangladesh, India, and Nepal continue to provide potable water for drinking and cooking within the WHO water quality limits.

**Keywords:** Arsenic Filter, Groundwater, Composite Iron Matrix, Sorption Dynamics.

411. Computer numerical control (CNC) milling for rapid production of poly(dimethylsiloxane) (PDMS) microfluidic devices

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With the benefits of reduced reagent volumes and analysis times, microfluidic devices offer an ideal platform for use in undergraduate research labs. Poly(dimethylsiloxane) (PDMS) devices, in particular, offer ease of fabrication and reduced cost relative to other microfluidic substrates. This work describes the use of a computer numerical control (CNC) mill to pattern molds for PDMS microfluidic devices using designs prepared with AutoCAD software. Variables examined include tool size, feedrate, and channel geometry. Devices are evaluated in response to both pressure-driven flow, using both on- and off-chip pumping, and voltage-driven flow, using electro-osmotic flow (EOF), to determine their viability in microfluidic analysis. Advantages and limitations of the fabrication technique are presented, with comparisons to more conventional processing methods.

412. Direct Mass Spectrometry Screening of Pomegranate Juice Adulteration

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Adulterations of pomegranate and other juices have been documented in the US market, including the addition of unapproved dyes and colorants. Because economic adulteration can often include the use of unsafe substitutes, and because it defrauds the consumer, testing needs to both catch adulteration before sale, and discourage future adulteration. Therefore adulteration testing needs to be easy, rapid, and reliable. Pomegranate juice (PJ) is highly prized by some consumers for anti-oxidant
and purported health benefits, and its price provides a high risk-reward ratio. Currently, testing juices such as PJ for adulteration requires performing 5-11 separate methods, requiring multiple sample preparations, analysts, and often days-weeks from sampling to results. A rapid pre-screening technique is needed to eliminate most of this laboratory effort (for authentic samples) and speed the time to results (for adulterated samples). Ambient ionization mass spectrometric (MS) analyses such as Direct Analysis in Real Time (DART-MS) allows for direct ionization and MS analysis of food samples without sample preparation. Since DART-MS analyses require no preparation and can take as little as 2 minutes per sample, DART-MS may be the best technique currently available to speed ongoing juice adulteration screening. A method to screen PJ for adulteration was developed and optimized using previously identified multi-chemical authenticity parameters. Method development also utilized previously authenticated as well as recently violative samples. Results to-date suggest DART-MS will provide significant cost/time savings, and dramatically speed sample throughput and time-to-results.

413. **Environmental Fate of Polyhexamethylene Biguanide**

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Polyhexamethylene biguanide (PHMB) is used as a bacteriocidal agent in a wide variety of applications, from pools and spas to medical devices. Although PHMB is not very toxic to mammals, it is highly toxic to aquatic species, such as trout and daphnia. Standard waste water treatment will likely degrade PHMB, but if spilled or dumped directly into water it can devastate aquatic organisms. The stability of PHMB in various aqueous solutions, surface water, soils, and on concrete was examined. PHMB was not significantly hydrolyzed in most aqueous solutions, however, bound immediately to soils, with the exception of sandy soil. Weathered concrete samples soaked up PHMB rapidly, and subsequent attempts to leach the PHMB out of the concrete failed. In addition, one over the counter wound care product containing PHMB was evaluated in water and soil to assess leaching capabilities. Although very stable in water, PHMB is likely not a significant threat to aquatic organisms as it binds to soil and concrete.

414. **Ultra-sensitive detection and effect of Hg(II) on cell membranes**

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Methods for measuring concentration and effect of Hg(II) on cell membranes were developed and tested. A high-precision technique, which integrates electrochemical magnetohydrodynamics (EC-MHD) and surface plasmon resonance (SPR), has been developed to detect Hg(II) ions down to 1 femto molar concentration in aqueous solutions. During the detection of Hg(II) ions in an aqueous solution using SPR and electrochemical technique, an electrical current is transmitted through the solution due to the potential applied during the deposition and the stripping steps. The presence of a magnetic field applied externally generates the Lorentz force that induces fluid motion, which in turn enhances considerably the mass transport of the Hg(II) ions toward the working electrode without any use mechanical stirrers or rotating electrodes. A new technique combining radiochemistry and fluorescence has been developed to measure the effect of Hg(II) on the permeability of cell membranes. \(^{203}\)Hg was used to measure the uptake of Hg(II) and fluorescamine was used to measure the efflux of amino acids from the cell membrane. Results show that both Hg\(^{2+}\) and MeHg\(^{+}\) are effective in disrupting the permeability of cell membranes, causing leakage of essential amino acids from the cells.

**Keywords:** Mercury; Surface Plasmon Resonance; MHD, Uptake; Amino acid; Membrane
415. Argon and the pathophysiology of pulmonary oxygen toxicity

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Molecular interaction can be determined from biological experiments. In the case of dynamics at the atmosphere-lung interface the physicochemical and atomic attributes of inhalant gases have significant biological and pathogenetic consequences. Hyaline membrane disease (HMD) is a common and sometimes lethal disorder, especially in premature newborns. Current therapy includes artificial ventilation and increased oxygen in the inspired air, despite evidence the lesions can be induced by oxygen enrichment [Lab.Invest. 21:439, 1969]. Bilateral cervical vagotomy (BCV) is a standard method of inducing ventilatory distress which leads to HMD [J.Exp.Med. 66:397, 1937; Biol.Neonat. 6:340, 1964; Biol.Neonat. 11:61, 1967]. The lungs of post-vagotomy newborn rabbits show the lesions of HMD in extent directly proportionate to the percentage of oxygen in polybaric (0.2 - 3.0 Atm.Abs.) mixtures with nitrogen. Avery [Pediatrics 32:801, 1963] found that lesions of HMD did not form at very low levels of oxygen (3-4% in nitrogen) in various newborn animals, suggesting that inhalant hypoxia was not a pathogenetic factor per se. The observation of lung injury proportionate to oxygen percentage indicates the physiological axiom of gas effects by their partial pressure is an artefact of sea level gas dynamics. The toxic effect of oxygen can be viewed as nitrogen lack. Some lung injury does occur when only 3 and 7 per cent oxygen in nitrogen is used, suggesting rather a specific oxygen effect. When nitrogen is replaced by hydrogen, helium, neon, argon, or sulfur hexafluoride, the extent of lesions often increases, indicating again a fundamental oxygen-nitrogen interaction. Low level studies with hydrogen and argon are especially instructive with and without BCV: (1) extremely long survival without BCV in oxygen-argon at 3% and 7%; (2) significant but less enhancement of survival at 3% oxygen in hydrogen without BCV; (3) no distinction in survival after BCV for 3% oxygen in nitrogen or hydrogen; (4) a pattern of lesion formation in the alternative gas mixtures which suggests nitrogen has a partially protective effect along with its stochastic competition for a common oxygen-nitrogen receptor or transmembrane port; and (5) generally, the mammalian lung is well adapted by evolution to current atmospheric composition but at the price of more inhaled oxygen than is required for cellular function [Perspect.Biol.Med. 13:80, 1969], allowing for toxic effects. The distinctions amongst these gases in the biologic sense are due to differences in their mass, monatomic or diatomic structure, possibly viscosity in air passageway flow, inherent energy state, and at low levels, in the electron saturation of the outer atomic shell. Unbuffered oxygen enrichment of air for ventilatory support is fundamentally injurious; hydrogen has obvious risks in a clinical setting but argon, which is abundant, non-flammable, and relatively non-toxic, may be the diluent gas of choice for ventilatory support.

416. Chemical paint strippers: Understanding how methylene chloride and phenol remove polymeric coatings

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Solvent paint strippers based on phenol and dichloromethane are effective and inexpensive yet pose severe environmental concerns. Attempts to replace them with equally effective, environmentally friendly alternatives have been unsuccessful. Consequently, the current paint stripper is investigated to develop a better understanding of the fundamental mechanism. This effort utilized commercial coatings, both primers and topcoats that meet military specifications, as well as control coatings made with reduced or no pigmentation. Use of simplified coatings enabled study by characterization
techniques that would have been impossible on a commercial coating due to the interference of pigments and fillers. Changes in molecular properties upon exposure to the individual solvents of the paint strippers were monitored by solvent sorption studies using a diffusion cell, TGA, DSC, FTIR, Raman, and solid-state proton and deuterium NMR. The results suggest physical swelling by dichloromethane and chemical reactivity by phenol that act together to delaminate the polymeric coatings.

417. Filtration of natural and synthetic estrogens using an activated charcoal solution

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The presence and effects of endocrine-disrupting chemicals (EDCs) such as natural and synthetic estrogens on animal and human populations has become a cause for concern. EDCs present in the environment have caused increased incidences of intersex marine vertebrates and elevated vitellogenin levels in male fish, as well as various malformations and adverse health effects in humans, such as hypospadias and cryptorchidism. It is imperative that methods of filtering or otherwise removing endocrine disruptors be created and implemented. One such promising method is that of activated charcoal filtration. In this study, the bioluminescent yeast estrogen screen (BLYES) developed by Sanseverino et al. was used to determine the estrogenicity of standard and experimental solution.

Experiments using a 10% activated charcoal solution achieved 99.1% and 79.3% reductions, respectively in the concentration of two known natural and synthetic estrogens, 17β-estradiol and bisphenol A.
Activated charcoal holds great potential for reusable and highly effective EDC filtration, but more experiments must still be performed to optimize this method and to enact widespread application.

418. Light-mediated oxidative decontamination on polyurethane coatings

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The decontamination of surfaces exposed to toxic chemicals is often a time-consuming and expensive process. This research demonstrates the development of a polyurethane coating that possesses the capability to continuously decontaminate harmful compounds by incorporation of surface segregating reactive additives into polymeric coating matrices. C60 fullerene was specifically selected to impart reactive capability to the coatings, as it is known to generate singlet oxygen upon illumination with visible light. The percent by weight of fullerene necessary to impart self-decontamination was optimized, while surface energy and glass transition were measured to ensure the performance characteristics of the coatings were maintained. The analysis of the degradation of surface residing organophosphate pesticides under various visible spectral regions and the detection of oxidation by-products both suggest singlet-oxygen mediated photocatalytic behavior. Additional evidence of the mode of action will also be presented.

419. Evaluation of lime-stabilized biosolids as a soil amendment

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Lime stabilization is a cost-effective method to treat wastewater sludge for destroying pathogens, reducing odor, mitigating metal leachability, and improving biosolids handleability. The resulting product – lime-stabilized biosolids, however, may contain extremely high alkalinity and relatively low available nutrients when used as a soil amendment in crop production. Extensive analyses were conducted to evaluate the fertilizer value and nutrient availability of lime-stabilized biosolids. Lime-stabilized biosolids obtained from a local wastewater treatment plant was analyzed for liming value and total and water-extractable nutrients. The material was further mixed with an acidic agricultural soil at 10 g kg⁻¹ (equivalent to 25 tons ha⁻¹) and leached intermittently with water for 6 months. Release of alkalinity and nutrients in leachate was continuously monitored. The soil acidity and exchangeable nutrients after leaching was also determined. The lime-stabilized biosolids had a fertilizer value of 4.0-0.8-0.2. Its CaCO₃ equivalent was 0.075 g g⁻¹. Amendment with the lime-stabilized biosolids at 25 tons ha⁻¹ eliminated the acidity of a pH 5.3 soil and provided plant-available nutrients at 162 kg N ha⁻¹, 12.3 kg P ha⁻¹, and 24.3 kg K ha⁻¹. Agronomic application rates of lime-stabilized biosolids were recommended in accordance with the results.

420. Removal of Chromium and Lead From Water by Sorption on Iraqi Montmorillonite

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Environmental site assessment of heavily destructed chemical process industries results in uncontrolled spread of heavy metals and toxic chemicals on land. The remediation of such polluted lands requires efficient methods for the removal of the pollutants. Chemical precipitation and adsorption are among the recommended procedures for this job. The present work describes a method for the removal of chromium and lead from water solutions by adsorption on a certified Iraqi clay stone,
montmorillonite. Response Surface Design (RSD) is employed in this study to evaluate the effect of operating parameters like the amount of clay in water (5 – 20 g/L), pH (2-7.5) of the solution and the treatment time (10-60 min). Batch equilibration experiments were carried out to follow the sorption behavior of Pb and Cr on the clay individually and in the presence of each other. The individual sorption experiments indicated relatively higher removal efficiencies of lead than for chromium. The most favorable sorption conditions were evaluated for both metal ions. The presence of lead with chromium influenced the sorption capacity of the two elements in different manner. The adsorption capacity of chromium is reduced by 35% and that of lead by 20%. However, the conditions that resulted in maximum lead adsorption are different from those of maximum chromium removal.

421. Thiol compounds that bind heavy metals

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Heavy metal pollution in aqueous environments is a serious threat to the human civilization. There is a global need to find a permanent and readily implemented solution to this problem. In an attempt to find a solution to this problem a number of thiol compounds have been synthesized and characterized. The first of them, benzene-1,3-diamidoethanethiol (BDETH₂), also known as \(N,N'\)-bis(2-mercaptoethyl) isophthalamide or \(N,N'\)-bis(2-mercaptoethyl)-1,3-benzenedicarboxamide has proven capable of binding divalent metal ions. A broad range of BDET-metal compounds has been prepared and characterized by IR, MS, EA, Raman, XAFS and TGA. The characteristics of the BDET-M compounds were determined through secondary reactions. In an effort to derivatize BDET-M compounds through alkylalumination a new cyclic compound, 1,3-bis(4,5-dihydrothiazolo)benzene, has been synthesized by refluxing BDETH₂ in the presence of AlMe₃ and fully characterized. Mineral coating studies have been performed and it was found that coating with BDET prevents metal leaching. XPS studies indicated that covalent bonds exist between BDET and the mineral surfaces. BDETH₂ is not water soluble and must be used as an ethanolic solution to precipitate metals from water. In an effort to find similar ligands that are water-soluble another dithiol compound, \(N,N'\)-bis(2-mercaptoethyl) oxalamide (MOA), and a monothiol compound, \(N\)-mercaptoethyl-furoylamide (MFA), have been synthesized. Each was found to precipitate Cd, Hg and Pb from water, to varying degrees. Some metal compounds of MOA, MFA and dithiothreitol (DTT), a water-soluble dithiol compound have been prepared and characterized. These compounds provide insight into the properties of the BDET-M compounds. For example, it is shown that insolubility in water is a common feature of thiol compounds and is not unique to BDET-M compounds.

Key words: Benzene-1,3-diamidoethanethiol (BDETH₂), heavy metal remediation, acid mine drainage (AMD), X-ray absorption fine structure (XAFS), X-ray photoelectron spectroscopy (XPS).

422. Catalytic Electrochemical Reduction of \(\text{CO}_2\) in Designed Ionic Liquid

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Carbon dioxide produced by consuming of fossil fuels is regarded as the most significant source of greenhouse gas. Meanwhile, \(\text{CO}_2\) is one of the most naturally abundant, inexpensive, non-flammable and non-toxic C₁ resources in chemical industry. \(\text{CO}_2\) is one of the reactants in the production of several important materials including urea, polypropylene oxides, and polycarbonates. In general, many of the syntheses using \(\text{CO}_2\) are conducted at relatively high pressure, elevated temperature, and the presence of catalysts. For the above reasons, it is essential to develop facile and inexpensive chemical methods to convert \(\text{CO}_2\) to usable materials under mild conditions (temperature and pressure).
Ionic liquids (ILs), composed merely of ions, are a kind of novel medium for many chemical processes. In recent years, significant progress has been made in the applications of ILs as alternative and more effective solvents, electrolytes, or catalysts. In the IL 1-methyl-3-butyl-imidazolium tetrafluoroborate (BMIMBF₄), CO₂ was reduced on a Cu electrode and a Ag electrode at -2.4 V vs. Ag/AgCl at room temperature and at -2.0 V vs. Ag wire at 50 °C, respectively.[1-2] In 1-methyl-3-butyl-imidazolium (BMIM+) acetate, the reduction potential of CO₂ was found to be -1.8 V vs. Ag wire at room temperature.[3] In the IL BMIMPF₆, supercritical CO₂ was reduced at high pressure (8.5 MPa) in the presence of water.[4] Extreme temperature, high pressure, and extremely negative potentials are not counterindicated with respect to energy consumption and the special equipment required. In this work, an IL 1-ethyl-3-methyl-imidazolium trifluorochloroborate (EMIMBF₃Cl) with a novel anion (BF₃Cl⁻) has been used. It was found that CO₂ gas can be dissolved and electrochemically reduced at ambient pressure, and room temperature in the ionic liquid EMIMBF₃Cl. The reduction of CO₂ occurred at a relatively less negative electrode potential of -1.8 V vs. silver wire. The reduction current density can be as high as ~5.7 mA/cm².


423. Interactive internet database cataloguing descriptive information about botulism cases since 1793

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Each year, there are more than 100 cases of botulism in the United States that are reported to the National Botulism Surveillance System (Centers for Disease Control and Prevention, Council of State and Territorial Epidemiologists). A small number of these cases resulted in death. In recent years, the most common cause for botulism in the United States is infant botulism, followed by foodborne and wound botulism, respectively. For this report, we have compiled a list of cases of either confirmed or suspected botulism from various locations around the world since 1793, from sources including PubMed (National Center for Biotechnology Information), ProMED-mail (International Society for Infectious Diseases), and Morbidity and Mortality Weekly Reports (CDC). A brief description of the circumstances surrounding each case is given, along with geographical information, when that information was available from publicly accessible sources. This compilation of data is part of a larger study to create an interactive internet database cataloguing date, geological location, outcome, and other descriptive information about botulism cases in the United States and worldwide.

424. Determination of biologically active compounds in green tea dietary supplements

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Green tea (Camellia sinensis) is purported to have a variety of health benefits due to its wide range of organic, biologically active compounds. The potential health benefits of green tea have been attributed primarily to catechins, which are polyphenolic antioxidants that reduce the effects of oxidative stress in the body. While epigallocatechin 3-gallate is the most prevalent, there are at least six other catechins present in green tea including catechin, gallo catechin, epicatechin, epigallocatechin, gallo catechin 3-gallate, and epicatechin 3-gallate. Other notable organic constituents in green tea
include gallic acid, which is an antioxidant that may also promote weight loss, and theanine, which is an amino acid that has potential health benefits including reducing anxiety and lowering blood pressure. Green tea also contains the xanthine alkaloids caffeine and theobromine, which act as mild central nervous system stimulants, and theophylline, which is a bronchodilator.

Because of the perceived health benefits of its bioactive constituents, green tea is widely used in dietary supplements. The dietary supplement market has grown rapidly in recent years, creating a need for accurate measurement methods for the bioactive ingredients and standards that are well-characterized with regards to the identity and amount of the major constituents. To address the need for measurement standards, the National Institute of Standards and Technology (NIST) is working in collaboration with the National Institutes of Health, Office of Dietary Supplements (NIH-ODS) to develop dietary supplement Standard Reference Materials (SRMs). Unprocessed, extracted, and/or processed forms of the dietary supplements are prepared that represent different analytical challenges. For green tea, NIST has developed three Standard Reference Materials (SRMs) including SRM 3254 *Camellia sinensis* Leaves, SRM 3255 *Camellia sinensis* Extract, and SRM 3256 Green Tea-Containing Solid Oral Dosage Form. Methods were developed for determining catechins, gallic acid, theanine, and the xanthines in each SRM using liquid chromatography with ultraviolet absorbance and/or electrospray ionization mass spectrometric detection. The SRMs are intended primarily for use in method development and as control materials to support the measurement of these constituents in green tea dietary supplements as well as other similar products.

425. Membrane bioreactor process modeling and optimization by Artificial Neural Network and integrated bioprocess models

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The energy efficiency of Ulu Pandan MBR plant is optimized by Artificial Neural Network (ANN) and bioprocess models. The ANN model predicts the dependence of the energy consumption per unit permeate product on operating parameters. The input variables for the ANN model are the volume of membrane scouring aeration, the volume of bioprocess aeration, the volume of mixed liquor transferred into the MBR system, and the volume of treated water produced. The input variables are used by the ANN model to predict the dependent output variable, energy consumption per unit permeate product water (kWh/m³). The ANN model results correlate well with operating data. An integrated bioprocess model based on the Activated Sludge Model is developed that includes the effects of sludge retention time (SRT), bound extracellular polymeric substances (EPS), and soluble microbial products (SMP). The bioprocess model investigates the impact of SRT on biological parameters in the bioreactor. The bioprocess model predictions of the key performance indicator, concentrations of SMP in the bioreactor, agree well with experimental results.

Within Ulu Pandan Water Reclamation Plant (WRP) is an MBR plant with a design flow rate of 23,000 m³/day. The cost for operating the MBR system stems predominantly from its overall power consumption. The owners and operators of the MBR system, Public Utilities Board (PUB) and Centre for Advanced Water Technology (CAWT), desire to reduce its power consumption from 0.55 kW-hr/m³ to 0.4 kW-hr/m³ (reduction of 27%) to achieve directly correlated cost savings.

The strategy for cost savings is to develop computational models of the MBR system that will:

(a) Identify optimal operating conditions from mining of data of the system performance

(b) Provide in-depth understanding of underlying the biological processes that are occurring within the MBR system and then identify optimal biological conditions.
The model of Item (a) is developed using Artificial Neural Networks (ANN). The ANN model performs data mining of previous plant operating records to determine the optimal operating settings within the ranges that have been historically practiced.

The model of Item (b) is developed using mechanistic bioprocess kinetics and is based on the standard Activated Sludge Model (ASM) series. The bioprocess model provides rigorous understanding of the biological processes occurring in the system and how those processes change with adjustments to operating conditions. From this detailed view of the bioprocesses, the model can then identify biological conditions that will even further improve the cost savings of the MBR system beyond levels achievable by the ANN model.

426. Application of GC-MS and Deconvolution Reporting Software for screening of organic contaminants from wastewaters

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In this study we developed a GC–MS protocol for the analysis of GC-amenable organic contaminants in wastewaters. Fourteen main municipal and industrial wastewater discharge points (Hyderabad, Pakistan) were selected for sampling in the first week of January 2010. Samples were preconcentrated/cleaned by employing solid phase extraction with HLB type cartridges. Analysis was performed in the scan mode, so that simultaneous screening of hundreds of compounds can be achieved followed by unveiling data with Deconvolution Reporting Software (DRS) using EPA and main libraries from NIST. Search was further refined if chromatographic peak pattern does not match for minimum three qualifier ions. Identified compounds were classified on the basis of functional groups and one compound from each group was used as surrogate to calculate response factor using anthracene as internal standard. Detection and quantification limits for each compound were also established.

Comprehensive analyses of wastewater samples from various sampling points indicated the presence of a large number of different organic compounds with a predominance of following main groups of contaminants; phthalates, esters, saturated aliphatic, cyclic and aromatic alcohols, mercaptans, benzene derivatives, saturated and unsaturated aliphatic and aromatic acids, saturated, unsaturated and cyclic ketones, aromatic aldehydes, higher alkanes and alkenes, aromatic homo/hetro hydrocarbons, organophosphorous, organo disulfides, organo chlorines, amides, amines and imines etc. Most of the compounds were detected at concentration levels ranging from 0.45 to 1000 ng/L and from 1.2 to 3472 ng/L in effluent wastewater and river waters, respectively.

427. Process Optimization of the Synthesis of Ne-mPEG-L-lysine Hydrochloride by At-line Reaction Monitoring

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Small molecule process optimization by the use of in-process chromatographic methods is commonplace, but the use of such methods for the development of a synthesis of a polymer has typically not been reported. By the integration of process chemistry and analytical chemistry, the yield, solvent usage and operability of a two-step sequence for the synthesis of Ne-mPEG-L-lysine hydrochloride was accomplished. Chemical yields increased from 78% to 93%, hazardous solvents were eliminated and a two-step process was reduced to a one-pot preparation. mPEG reagents are finding increasing use in drug synthesis (Macromolecules, 2009) and in the pegylation of small molecules (Green Chemistry Letters and Reviews, 2008) as the incorporation of a mPEG polymer into a drug imparts beneficial therapeutic effects.
The present report represents a comprehensive study of the effect of poly(ethylene) glycol (PEG) degradation during electrolytic copper plating on the sporadic void formation at the Cu/solder interface. A thorough chemical analysis of our plating solution taken at different times of the deposition process carried out by matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectroscopy, reveals a dramatic shift in the peaks to lower mass range as the plating progresses over time. The corresponding SEM cross-sectional images of Cu samples that are plated at the corresponding times of the solution aging show a decrease in the sporadic voids formation at the intermetallic compound (IMC) due to lower molecular weight PEG incorporating into the growing Cu layer. These results show that PEG loses its suppression effect as it breaks down to lower molecular weight. We also report in this study on the effect of scaling up the experiment on PEG degradation in which comparative experiments are done using 50 mL bath volume in a rotating disc electrode (RDE) set up versus a scaled up experiment using the larger cell with a volume of 267 mL. The results show that PEG degrades at heavily accelerated rate in the plating bath with higher amount of the solution despite the two baths having the same charge/volume ratio. Overall, this work illustrates the critical importance of a detailed chemical analysis for the understanding of reliability issues of high importance in the electronics industry.

The liquid-liquid partitioning process for separation of molecules has been embodied in many instruments over the years. The instruments and apparatus include countercurrent distribution and droplet countercurrent chromatography and more recent ones, such as centrifugal partition chromatographs and the multi-layer coils in the planetary centrifuges. These are all methods of countercurrent chromatography (CCC). In CCC carried out in the open flow-tubing coils rotated in planetary centrifuges, there is a new design where spirals of tubing are more spread out. Recently, Yoichiro Ito, at the National Institutes of Health, invented a spiral plate assembly with widely spaced flow channels that could hold more viscous solvent systems which are optimal for high MW bio-molecules. This was the first rotor for spiral CCC. Now the spiral flow has been made possible in continuous tubing held in a frame. The wide spacing between the tubing significantly increases the stationary phase retention. Now all types of two-phase solvent systems can be used for chromatography. A spiral tubing support (STS) frame with circular channels was constructed by laser sintering technology into which FEP tubing was placed in 4 spiral loops per layer from the bottom to the top and a cover affixed allowing the tubing to connect to flow-tubing of the planetary centrifuge. The figure below shows the STS rotor mounted inside a planet centrifuge. The total volume of the coil is 135 ml.
Applications of this new separation rotor were developed. Examples of compounds of molecular weights ranging from <300 to approximately 15,000 were chromatographed in appropriate two-phase solvent systems to assess the capability for separation and purification. A mixture of small molecules including aspirin was completely separated in hexane-ethyl acetate-methanol-water. Synthetic peptides including a very hydrophobic peptide were purified to a very high purity level in a sec-butanol solvent system in preparative purification experiments. Sample loads of up to 100 mg were possible. In the STS rotor, high stationary phase retention was possible with the aqueous sec-butanol solvent system at a normal flow rate. Two-phase solvent systems with this alcohol are not well retained in multi-layer coils available in instruments of other manufacturers. Finally, the two-phase aqueous polyethylene glycol-potassium phosphate solvent system was applied successfully to separate a protein from a lysate of an E. coli expression system. These experiments demonstrate the versatility of spiral CCC to purify all types of molecules.

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430. Kinetics of Swelling of Crosslinked Amino-Functionalized Polysiloxanes. Possible Applications for Chemical Spill Containment and Remediation

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Previously, we prepared several types of ionically and covalently crosslinked amino-functionalized polysiloxanes (APSLs) by simple addition of CO₂ or CS₂ (and/or heating).[i] These APSLs were shown to imbibe large volumes of several organic liquids, especially those of low polarity. Here, we report a detailed investigation of the swelling and deswelling kinetics at different temperatures using neat and mixed solvents using a Fickian diffusion model.[ii] The swelling property can be tuned by varying the degree of crosslinking (i.e., the frequency of amino functionalities along a polymer chain). These investigations allow the rate-limiting step for entry into or exit from APSLs to be identified. Furthermore, the swelling/deswelling cycle could be repeated at least 3 times without significant loss of swelling capacity. Based upon these observations and the density of the polymers, a procedure for recovery of oils or chemicals from spills that includes reuse of the APSLs has been developed. As such, it may be a facile method for chemical spill containment and remediation.

We thank the National Science Foundation for its financial support of this research.

The interaction of terahertz radiation with a given molecule is greatly influenced by the characteristic parameters of the molecule such as its molecular weight, various vibrational modes, and the presence of attenuating entities such as water. As such, terahertz transmission (or equivalently terahertz absorption/reflection) is a function of the concentration of each species present. This hypothesis has been successfully tested on macromolecular systems [1]. In the present work, terahertz spectrometry was used to further characterize the spectral features and measure the sensitivity of detection of non-ionic detergents and purified protein in aqueous solution [2]. A comparison of terahertz and IR spectra for several compounds will be provided, demonstrating the significant increase in spectral detail available with terahertz illumination versus IR. The attenuating effect of water on terahertz transmission was measured in a short path-length cuvette using aqueous dilutions of liquid detergents Tergitol™ NP-9 and Triton X-100. Details of these findings will be presented with exemplary data.


Infrared-visible sum frequency generation (SFG) vibrational spectroscopy and complementary surface analytical techniques were employed to characterize the structure of amino-terminated organic thin films on solid substrates. Amino-terminated organic films were prepared on silicon oxides by self-assembling 3-aminopropyltriethoxysilane (APTES) in anhydrous toluene for varied deposition times. Ellipsometric measurements showed that the thickness of APTES films increased with the deposition time, but was subsequently reduced after curing at 100 °C for 24 h. SFG spectra from APTES films contain signals corresponding to both CH- and NH-stretching modes, but their intensities depend on the deposition time and curing. The intensity of the CH stretching modes located between 2850 and 3000 cm⁻¹ increased as the thickness of APTES film increases, but significantly attenuated after curing. In addition, the signal intensity of the NH stretching mode around 3290 cm⁻¹ in SFG data was not clearly observed before curing regardless of the film thickness, but it was apparent in the spectra after curing. Our SFG data suggests that the hydrophobic ethoxy groups were aggregated on the surface before curing, but these ethoxy groups were removed and the more hydrophilic amino groups were present instead. This is supported by independent Fourier transform infrared spectroscopy (FTIR) studies and reactivity assessment of surface amino groups in APTES thin films via fluorescence measurements.
From Local to Global Vibrational Modes: What Terahertz Spectroscopy Tells Us About Protein Folding

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Our healthcare system is increasing confronting a rise in protein misfolding diseases such as Alzheimer’s disease (AD), Parkinson’s, and Huntington’s disease. These diseases exact a devastating toll on patients and their families, resulting in severe impairment of social and physiological functions leading to an earlier expiration. While some progress has been made in ameliorating the deleterious effects of AD, our fundamental understanding of processes leading to AD is seriously lacking. In particular the role of water in Aβ aggregation and aggregate disassembly remains largely unknown. The far-infrared Terahertz radiation spanning the region 0.1 to 1 mm is exquisitely sensitive to coupled motions of protein and water. Coupling of water to protein global modes can enhance dipole moments and yield strong THz signals. It is therefore possible to selectively study biological water using THz spectroscopy. In our on-going THz studies of model peptide-water systems, we have used THz spectroscopy and quantum mechanical calculations to probe the coupling mechanisms of peptide-water interactions in dipeptides derived from Aβ40.


Terahertz Absorption Characteristics of Single Species Oligonucleotides

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The molar extinction coefficient, \( M \), of single species oligonucleotides in the UV range has been found to be in the order \( M_A > M_G > M_T > M_C \), where the subscripts stand for Adenine, Guanine, Thymine, and Cytosine, respectively [1]. While this is known, the nature of absorbance in the terahertz (THz) region remains unknown. Molecular structures may behave differently because of their resonance states depending on the region of the spectrum. Therefore, investigation of absorption in the terahertz region is of interest. Terahertz is particularly useful in the measurement and analysis of organic and biological molecules, as it senses the vibrations of entire molecules.

In this paper we studied single species synthetic nucleotides for their absorbance characteristics in the terahertz region. A terahertz spectrometer was used (TeraSpectra, Applied Research and Photonics, Harrisburg, PA) to measure the steady state transmittance of each nucleotide. Glass slides were cleaned and steady state transmission of the blanks was recorded as reference. It has been found that different slides of the same batch are not identical but have differences in transmission. The slides were then used to make four sets of sample each of A, G, T and C. Aliquot 20 µL of 68.833 µM solution of each nucleotide was dispensed on a slide with a micropipette. The slides were dried on a hot plate at 45°C for 15 minutes, having formed solid spots with distinct boundaries. The samples were then mounted on an XYZ stage and placed in the beam path of the spectrometer. Using the stage micrometers, each slide was positioned for minimal transmission. In this way the steady state transmission all 16 slides were recorded over the range of 0.1 to \( \sim 30 \) THz. The reference was then
subtracted from the slide samples to determine the absorbance of each sample: absorbance = transmitted power of blank glass slide – transmitted power of the same slide with nucleotide (spot) on it.

Fig. 1 shows the absorbance of individual samples along with the average values for all four nucleotides. Unlike in the UV region [1], the absorbance in the THz region follows the following order $M_A > M_G > M_C > M_T$. The measurements were repeated twice with the same outcome. Possible reasons of this apparent anomaly will be discussed.


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This presentation will provide an overview of a market analysis of terahertz systems performed by Thintri, Inc., that explores prime emerging markets for a range of terahertz-related technologies. Terahertz radiation, by virtue of its ability to penetrate so many materials that are opaque to the visible spectrum, has the potential of opening up markets in an astonishing array of applications. Terahertz technology can be implemented in a number of modalities: continuous wave or time domain; imaging or spectroscopy. Each has its advantages and liabilities, and suitable applications. In security applications alone, imaging can be used for airport security to detect hidden weapons or objects, while time domain spectroscopic systems can be used to detect materials of interest carried by passengers at parts per trillion levels.

Growth of markets has been hobbled by lack of funding for needed technology development, as well as premature hype of the capability of terahertz systems. However, technology has continued to progress and today, robust, relatively inexpensive and even portable terahertz systems are available commercially, suitable for many high profile applications. Industry players are preparing to enter widely varied markets, from security to medicine to manufacturing process control to wireless communications and others. Market opportunities within the decade are quite promising. A number of markets within medicine, security and manufacturing are likely to reach the hundreds of millions of dollars per year before 2020, leading to overall markets possibly in the billions.

436. Low Wavenumber States of Fullerenes Observed by Terahertz Spectrometry

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The Fullerenes $C_{60}$ and $D_2@C_{60}$ differ only by an encaged deuterium molecule for the later and thus difficult to distinguish their spectral features using standard spectroscopy methods. However, tera-
hertz (THz) interaction with macromolecules is sensitive to the vibrational modes of the entire molecule, as opposed to just a bond or its rotation. Thus, it is expected that broadband THz spectrometry should be able to discern the vibrational states of these two species. Here, Terahertz Time-domain Spectroscopy (TDS) was used to determine the features in the respective spectra of the above two fullerenes. A transmission-mode terahertz spectrometer (TeraSpectra, Applied Research & Photonics, Harrisburg, PA) was used to characterize the specimens.

The absorbance spectra of C₆₀ and H₂@C₆₀ were examined recently [2]. It was found that there are several absorbance peaks present in the THz spectra that were not seen by the IR spectra. This is indicative of the sensitivity obtainable from THz interaction with the entire molecule. The presence of multiple states in the low frequency region observed at room temperature indicates that the vibrational states of these molecules can be effectively probed by THz.

It has been predicted by Turro et al. [3] that an important ability of the Fullerene research is the possibility of controlling the spin selectivity of the catalyzed conversion of para H₂@C₆₀ into ortho H₂@C₆₀ so that a strong nuclear spin polarization is produced. However, if spin selective H₂@C₆₀ is synthesized, it will be difficult for standard IR spectroscopy to distinguish and identify the ortho and para species. The presence of distinguishable absorbance peaks identified by THz spectra [2] suggests that this tool has the required sensitivity for detecting the spin isomers of H₂ inside C₆₀. Additionally, the presence of additional peaks indicates that this method can detect modes not visible in standard IR or Raman, yielding unique insight into uncharacterized host/guest interactions.

For the present work, pure C₆₀ and D₂@C₆₀ were used. Gravimetric method was used to make solutions of as received samples (in powder form). In particular, 5.09 mg C₆₀ was added to 3.33863 g solvent (1, 2-dicholorobenzene), yielding a solution of 1.52458 mg/g. Similarly as received 4.31 mg D₂@C₆₀ was dissolved in to 2.83502 mg solvent resulting 1.52027 mg/g solution. 30 µl of each solution was dispensed on two glass slides. The slides were dried and mounted on a XYZ stage one at a time; their spectra were acquired by the TeraSpectra front-end. It is expected that these spectra will allow comparing the vibrational states of D₂@C₆₀ with those observed for C₆₀ and H₂@C₆₀. Dideuterium (D₂) has a rotational constant that is half of H₂ (~30 cm⁻¹ versus 60 cm⁻¹), so one should see one or more of the lines shift by some meaningful frequency. The acquired time-domain data will be analyzed and some details will be discussed in this presentation.

2. Anis Rahman, Michael Frunzi, Aunik Rahman and Nicholas J. Turro, “Vibrational States of C₆₀ and H₂@C₆₀ in Low Wavenumber Region Observed by Terahertz Spectrometry,” to be submitted.

437. Single Nucleotide Polymorphism Detection via Terahertz Spectrometry

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Spectrometry is the key technique to investigate all kinds of molecular characteristics. However, two important factors for effective characterization of molecular phenomena are the sensitivity and the penetration depth. The better the sensitivity, the smaller is the sample requirement; and the deeper the penetration, the richer the information that can be extracted. From these and other considerations, terahertz (THz) radiation has the right kind of properties for information-rich spectroscopy applications. Simply put, while all other wavelengths are sensitive to either a bond, rotational or torsional vibrations, terahertz wavelengths are sensitive to the vibrational modes of an entire molecule.
or a macromolecule. This is the basis of very high sensitivity response of THz interaction with molecular system. Because of its longer wavelength, THz can penetrate deeper into substrates compared to visible or IR light. Because THz radiation does not suffer from ionization loss, it can also penetrate deeper in a substrate.

Single nucleotide polymorphisms (SNPs) are DNA sequence variations that occur when a single nucleotide (i.e., A, T, C, or G) in the genome sequence is altered. SNPs make up about 90% of all human genetic variation and SNP detection and genotyping are of fundamental importance in the identification of numerous genetic and hereditary diseases and also for the development of personalized medicine [1].

Current methods for SNP detection require PCR amplification, DNA denaturizing, and fluorescent labeling. DNA sequences are identified by hybridization of unknown target DNA molecules to known single-stranded probe molecules. However, fluorescent labeling introduces modifications in DNA strand conformation that lower the accuracy of gene detection. Label degradation, labeling yield fluctuations, fluorescence efficiency site dependence and fluorophore quenching inhibit the quantifiability of genetic diagnostics. In contrast terahertz spectroscopy can be used to identify DNA hybridization without labeling. Because of its very high sensitivity, it is expected that one should be able to extend the method for establishing a distinctive signature of any individual double-stranded pair of (pure) oligonucleotides, including hybridizations of designed oligonucleotides targeted to bind specifically to particular SNPs, and possibly pick out this signature even against a complex background including both other variants of the same SNP (e.g., on the other allele of the same gene) as well as a general dsDNA background. In this effort we examine the feasibility of THz route to identify the main challenges for future directions.

Single Nucleotide Polymorphism of 21-mer synthetic oligonucleotides has been investigated by terahertz spectrometry. Spectra up to 15 THz obtained from the measured time-domain pulse of 559T>G SNP of FCGR3A gene exhibit clearly distinguishable features. Strand 559G has higher absorbance than its SNP 559T. This is explained by the higher absorbance of the guanine alone compared to thymine alone. Future work is aimed at identifying the different hydrogen bonding that is responsible for the formation of the nucleotide pairings in double-stranded DNA. Such ability in turn will allow sequencing of DNA without labeling and amplification.


438. Quantitation of gaseous pollutants at ppm concentrations using THz-TDS

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Advances in semiconductor and ultrafast laser technologies in recent decades have enabled development of improved terahertz (THz)-frequency (~2 – 200 cm⁻¹) technologies. The current generation of instrumentation has renewed interest in the THz frequency range, in part due to increased signal-to-noise ratios, lower maintenance needs, and expanded commercial availability. Though many gaseous species exhibit absorption features in this spectral range, scientific literature covering quantitative analysis with the current generation of THz spectrometers has been sparse. These absorption features correspond to fundamental molecular rotational transitions. Increased chemical selectivity should be available, as the spectral features represent the structure and composition of the species, rather than intra-molecular functional groups. Electromagnetic waves at these frequencies are non-ionizing, making exploitation for atmospheric measurements safe.

This presentation will focus on our efforts to use a commercially available THz time-domain spectrometer (TDS) for the characterization and quantitation of ammonia (NH₃), water vapor (H₂O), and...
acetonitrile (CH$_3$CN). Permissible exposure limits of 50 and 40 ppm have been set for ammonia and acetonitrile, respectively. These limits set a feasibility target for the use of this apparatus for such an application. Each species was chosen to highlight different characteristics in the predictive performance of the apparatus. Water vapor is ubiquitous in the atmosphere and has a strong absorption spectrum at these frequencies, necessitating inclusion as a potentially confounding matrix element. Absorbance features associated with water vapor are highly overlapped with those of ammonia in this frequency range, providing an opportunity to explore measurement selectivity. Both species are also relatively strong absorbers of THz radiation, whereas the absorptivity of acetonitrile is much lower. Absorbance features associated with acetonitrile are well separated from those of the other two species, so the quantitation of this species will primarily test the sensitivity of the apparatus.

The effect of overall pressure on spectral features associated with each species was investigated from ~233 – 799 torr (0.31 – 1.05 atm, 31 – 106 kPa), representing pressures expected for surface-based measurements. Each species was also prepared at part-per-million (ppm) concentrations at 760 torr (1 atm, 101 kPa) overall pressure for quantitative analysis. Quantitative analysis of the data was performed with classical least-squares (CLS) in the form of Beer-Lambert plots. Parameters from the regression allow an assessment of sensitivity and linearity across the calibration range. Partial least-squares (PLS) regression was also used to analyze the same data and assess the analytical utility of the method. Results from the PLS analysis of sample mixtures are equivalent to those of the pure components, illustrating the chemical selectivity of the method, despite spectral overlap.

439. **USP spectroscopic identification tests**

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USP is replacing outdated technology and methodology with more current procedures. Many of the identification (ID) tests utilize spectroscopic absorption techniques, such as FT-IR. Sampling is an important consideration when choosing a particular FT-IR method. Sometimes slight differences in spectra may be observed with different sampling methods KBr pellet and nujol, and different FT-IR techniques, such as DRIFTS and ATR. Therefore, it is important to specify the method and technique. Raman and Near IR should be considered complimentary techniques to FT-IR. A particular sample may be more sensitive to a complimentary technique than to FT-IR, and/or some labs might have limited instrumentation. Identification of a sample (API, food ingredient or excipient) is important, and the ability to determine if there are impurities or adulterants present in a sample is equally important. Would a spectral library be a solution?

**Drug Discovery**

Organizer: C. J. Thomas

440. **Molecules containing reactive peroxide or nitric oxide species for the treatment of malaria**

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Malaria continues to be an epidemic in developing countries, and parasite resistance to existing treatments remains a constant threat. It is therefore imperative that new treatments are continually sought, ideally those that can target a number of different pathways exclusive to the parasite. Pro-
liferation of malaria parasites is known to involve several redox pathways, affording the opportunity for redox-active molecules to interfere with such proliferation. To that end, molecules based on the natural product artemisinin (1, Figure 1), which contains a reactive peroxide linkage, have been developed that enhance the innate activity of the structure as demonstrated by improved (over existing dosing regimens) curative results in mice. More recently, molecules that generate nitric oxide have shown activity against a variety of parasitic diseases, including malaria. A nitric oxide-generating furoxan ring (2, Figure 1) has been hybridized with known antimalarial compounds such as chloroquine and amodiaquine in an attempt to target multiple redox pathways while also blocking resistance against similar quinoline-like molecules. Several mechanisms of action for both artemisinin and nitric oxide have been proposed, though each is thought to target separate pathways. The biological results show that artemisinin continues to be an important chemotype from which new antimalarials should be developed, and that nitric oxide donor hybrids represent a potential new class of drugs.

441. Exploration of the Existing Drug Space for Novel Inhibitors of Angiogenesis

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The discoveries of novel pharmacological activity of known drugs, sometimes referred to as the “off target” effects, have appeared in the literature from time to time. Recent years have witnessed an increase in frequency of the appearance of such discoveries. Finding new pharmacological activities for existing drugs offers a number of advantages. First, since existing drugs are already in use in humans, they are bioavailable and have tolerable side effects. Second, the well-established toxicity and bioavailability of known drugs in humans will significantly reduce the time and cost to evaluate drugs in the new indications in humans. Last but not least, the extensive knowledge on the mechanisms of action of known drugs and the availability of a large number of analogs during the development of each drug will significantly facilitate the understanding of the molecular basis of the new pharmacological activity and enable rapid structure/activity relationship study to develop new generations of the drug in the context of the new indication. Together, the advantages of this approach call for a systematic effort to collect and screen available FDA-approved drugs for new pharmacological activities. We began a new initiative to systematically collect and assemble a library of clinical drugs in 2003. To date, we have to date collected over 2,400 existing drugs and over 600 drug candidates and assembled them into the Johns Hopkins Drug Library. We have screened this library in a number of cell-based assays for new anti-angiogenic and antitumor agents. Novel and unexpected hits have been identified in each of the screens performed. Mechanistic deconvolution of those hits has shed new light on the regulation of proliferation of endothelial and cancer cells. Moreover, some of the hits have been shown to be efficacious in blocking angiogenesis and tumor growth in vivo, suggesting that they are promising leads for development into novel anticancer drugs.
442. Optimization and biophysical characterization of small molecules that inhibit influenza virus replication via binding to nucleoprotein (NP)

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Worldwide seasonal influenza epidemics are responsible for 250,000-500,000 deaths per year, yet the therapeutic options (i.e. vaccines, neuraminidase inhibitors, M1 channel blockers) have remained static for over a decade, even in the face of mounting viral resistance. New antiviral targets are clearly needed. In a parallel effort to that described by Kao et al. (Nature Biotechnology 2010, 28, 600-605), we identified compound 1 as a promising lead with potent antiviral activity against the A/H1N1/WSN/33 strain of influenza. Resistance mapping implicated nucleoprotein (NP) as the viral target for this chemotype, and site-directed mutagenesis experiments provided additional information about the putative ligand binding site(s). In this presentation, we report the optimization of 1 to afford analogs with improved aqueous solubility and metabolic stability, which facilitated the detailed biophysical characterization of the NP:ligand complex and confirmation of antiviral activity in a mouse model of influenza.

443. Discovery of N-type calcium channel (Ca$_{2.2}$) blockers for the treatment of chronic pain

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The ability of a Ca$_{2.2}$ calcium channel blocker to produce relief for intractable pain was established with the registration of Prialt® (ziconotide), a synthetic peptide that blocks Ca$_{2.2}$ channels following intrathecal administration. Ziconotide is a state-independent blocker and therefore blocks Ca$_{2.2}$ channels under all conditions and levels of activity, which produces a limited therapeutic index over psychiatric and neurological side effects. We sought to discover orally available, state-dependent Ca$_{2.2}$ blockers that might afford analgesic efficacy without ancillary neurologic activity. Our efforts afforded the structurally distinct calcium channel blockers Trox-1 and compound 2, illustrated below. This presentation will focus on the structure-activity optimization that lead to these compounds, and the resulting preclinical pharmacology associated with state-dependent calcium channel blockers.
444. The NIH Therapeutics for Rare and Neglected Diseases Program

John McKew(1), john.mckew@nih.gov, 9800 Medical Center Drive, Rockville MD 28092, United States. (1) Therapeutics for Rare and Neglected Diseases, NIH Chemical Genomics Center, Rockville MD 28092, United States

The National Institutes of Health (NIH) Therapeutics for Rare and Neglected Diseases (TRND) program, http://trnd.nih.gov is a congressionally mandated program to encourage and speed the development of new drugs for rare and neglected diseases. This unique program creates a drug development pipeline within the NIH and is specifically intended to stimulate research collaborations with academic scientists, non-profit organizations, and pharmaceutical and biotechnology companies working on rare and neglected illnesses. The TRND program provides an opportunity to partner with, and gain access to, drug development scientific capabilities, expertise, and resources in a collaborative environment with the goal of moving promising therapeutics into clinical testing.

This talk will provide an update on several of the TRND pilot projects. Highlights of these collaborative projects will include the progress made on advancing the Hereditary Inclusion Body Myopathy (HIBM) project and the Sickle Cell Disease project.


Organizers: K. Bianco, J. Hasford


Shana Cyr(1), shana.cyr@finnegan.com, 901 New York Ave. NW, Washington DC 20001, United States. (1) Finnegan, Henderson, Farabow, Garrett & Dunner LLP, Washington DC 20001, United States

In order to maximize patent protection, the claims of a patent should be as broad and all-encompassing as possible under the law. This presentation will provide an overview of the legal requirements for obtaining and maintaining patent protection and will discuss how to maximize patent protection within the confines of the law.

446. Drafting winning patents that withstand written description and enablement challenges

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Written description and enablement are two distinct requirements for a patent. To meet the written description requirement, the patent must disclose sufficient details such that an ordinary person of skill would believe that the inventor(s) had possession of the invention at the time of filing the pat-
ent application. To meet the enablement requirement, the patent must provide sufficient instructions such that an ordinary person can make and use the invention without undue experimentation.

Applicants for pharmaceutical patents face unique challenges to meet these two requirements: (1) what is the appropriate timing for filing a patent application and (2) what level of detail should be disclosed in the specification. This presentation will address these questions with an illustration of Federal Circuit cases.

447. Patenting chemical products and processes – how double patenting can limit patent protection

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An inventor can separately obtain patents on chemical products and the processes used to make them. However, the judicially-created doctrine of obviousness-type double patenting can limit that patent protection. This presentation will provide a brief introduction to the concept of obviousness-type double patenting and highlight recent cases in which the doctrine was applied.

448. Damages for infringement of chemical patents

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This presentation will involve a brief look at the evolution of damages in chemical patent cases. It will also include an emphasis on how recent case law may affect damages for chemical inventions, and how that may impact the future of chemical innovation.

449. Patent term extensions after drug approval

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Drug manufacturers may lose a substantial amount of patent term while waiting for FDA approval of their drug. To deal with this problem, the United States enacted the Hatch-Waxman Act. Several other countries provide similar protection that allow manufacturers to extend their patent term based on regulatory delays. An overview of the Hatch-Waxman Act will be discussed as well as the similarities between the U.S. system and those in other countries.

450. Pharmaceutical patent timelines

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Between 2010 and 2014, patents involving branded pharmaceutical drugs with over $209 billion in annual sales are projected to expire. In this presentation, I will address the timeline of a typical innovative drug patent. I will further discuss innovations that pioneer pharmaceutical firms recently have pursued.
451. Reconciling patent rights and public health issues: Implications of the TRIPS Agreement for the pharmaceutical industry

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The TRIPS (Trade-related Intellectual Property Rights) Agreement made it compulsory for WTO (World Trade Organization) members, with few exceptions, to provide protection for pharmaceutical product and process patents. Prior to the Agreement, patent duration was significantly shorter in many developed and developing countries. In addition, many countries provided only process — but not product — patents, and therefore did not prevent the manufacture of patented products by a process of reverse engineering, where a different process or method from that which has been invented (and patented) is used. One of the exceptions to the rule, however, is compulsory licensing which permits a generic drug manufacturer to make, use, import, and sell (but not export) the patented pharmaceuticals without the permission of the patent owners. Compulsory licensing has led to a conflict between public health and access to these drugs and reduction of the market exclusivity that patent holders depend on.

452. Proposed U.S. patent reform

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This March, the Senate passed its version of the America Invents Act, and a similar bill is pending in the House to overhaul the patent system. Significant patent reform measures after nearly sixty years include a transition to a first to file system and a new post grant opposition system.

Catalysis
Organizer, Presiding: L. Sita

453. Development of Metallocene Catalysts for the Polymerization of Ethylene

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Development of metallocenes as catalysts for polyethylene manufacture will be reviewed with an emphasis on linear low-density polyethylene. Catalyst structure-polymer property relationships, as well as reactor operability will be addressed. In particular, this talk will focus on metallocene structure as it relates to short and long-chain branch incorporation. Evidence for different mechanisms governing the incorporation of monomers vs. macromers will be presented.

454. Dinitrogen complexes of chromium - structures and reactivity

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We have prepared two different N₂ complexes of chromium, namely the side-on bonded [({}^{13}NnCr)₂(μ-η²:η⁴-N₂)]_₃(μ-η²:η⁴-N₂) (^{13}Nn = bis(2,6-diisopropylphenyl)pentane-2,4-ketiminate, and the end-on bonded [Tp^{Bu,Me}Cr]₂(μ-N₂)(μ-N₂) (Tp^{Bu,Me} = hydrotris(3-t-butyl,5-methyl-pyrazolyl)borate. Both complexes are rare synthons containing chromium in the formal oxidation state +I. The two molecules will be compared and contrasted with regard to their structures, properties and selected reactivity with small molecules such as O₂, ethylene, alkyls azides, etc.
455. High-valent manganese-oxo corrolazines in hydrogen-atom-transfer and oxygen-atom-transfer

David P. Goldberg

This talk will focus on our recent work involving high-valent manganese-oxo corrolazines. Corrolazines (Czs) are ring-contracted porphyrinoid ligands designed to stabilize high oxidation state transition metal complexes. The Cz ligand platform has allowed us to isolate a rare example of an Mn(V)-oxo complex. The reactivity of this complex, and related high-valent Mn complexes, will be described. Reactions that are of fundamental importance for both biology (e.g. heme enzymes) and for synthetic catalysts involve oxygen-atom-transfer (OAT) and proton-coupled electron-transfer (PCET). The (Cz)MnV-oxo complex exhibits both OAT and PCET reactivity, and mechanistic analyses involving the assessment of products and kinetic parameters for these processes will be presented. For example, C-H activation mediated by the (Cz)MnV(O) complex is shown to proceed through a PCET mechanism, and much of the driving force for this reaction appears to come from the affinity for the proton, or in other words, the basicity of the metal-oxo unit. We have also found that dramatic rate enhancements for C-H activation can be induced by exploiting our knowledge of the reaction mechanism, and kinetic data demonstrating these unprecedented rate enhancements will be presented.


Andrei N Vedernikov

Previously we reported a homogeneous PdII – 2,6-pyridinedicarboxylic acid system suitable for selective catalytic oxidative CH acetoxylation of some benzylic type substrates with O2 as direct oxidant.1 In this work we explore the relationship between structure of some novel PdII – pyridinecarboxylate complexes suitable for catalytic aerobic CH acetoxylation and their reactivity towards CH bond donors and O2. The substrate scope of these new catalytic systems will also be discussed.


457. Generation of NO at copper: Activation of organonitroso compounds and hydroxylamines

Timothy H. Warren

Nitric oxide is a versatile small molecule which plays an important role in numerous biological functions. While NO itself has a short lifetime (3 – 5 s) in the plasma due to ready reaction with O2 and O2-carrying enzymes, S-nitrosothiols RS-NO represent air-stable, circulating reservoirs of nitric oxide present at near micromolar concentrations. Additionally, RSNOs engage in transnitrosation (transfer of NO+) reactions with alcohols ROH and amines R2NH to give the corresponding O- and N-nitroso
compound RONO and R₂NNO. We describe our efforts to model the interaction of S⁻, O⁻, and N-nitroso compounds with copper model complexes inspired by prevalent histidine coordination in relevant copper enzymes involved in NO processing. We see that the coordination environment at copper plays a decisive role in the release of NO gas from these organonitroso compounds. Additionally, we outline reactions with hydroxylamines RNHOH that result in novel copper C-nitroso compounds [Cu] (η²-ONR). Such C-nitroso species serve as models for underexplored HNO (nitroxyl) redox congener of nitric oxide that is of intense biological interest.

458. Dinitrogen and carbon dioxide activation and fixation by groups 4 - 6 metal monocyclopentadienyl, monoamidinate complexes

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The unique steric and electronic features of the monocyclopentadienyl (η⁵-C₅R₅), amidinate {η²-[N(R₁)C(R₃)N(R₂)]} (CpAm) and guanidinate {η²-[N(R₁)C(NR₂)N(R₂)]} (CpGu) ligand environments are ideally suited for experimentally and computationally investigating groups 4, 5, and 6 early transition metal-mediated dinitrogen activation, N≡N bond cleavage, and N-atom functionalization within several isostructural series of CpAm- and CpGu-based dinuclear [LnM]₂(μ-N₂) complexes in which the nature of the metal center can be varied as a function of group and row position, formal oxidation state and dⁿ electron count. Mononuclear group 6 metal CpAm and CpGu terminal oxo and imido complexes have also been prepared from N₂O and CO₂ and organoazides, respectively. Facile oxo and imido group transfers involving these latter classes of compounds provide support for the development of catalysts that can employ ‘green’ chemical oxidants for the production of chemicals of industrial interest.

Redefining the Kilogram and Avogadro’s Number
Organizer, Presiding: R. L. Watters

459. The International System of Units and Plans for its Redefinition

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The International System of Units (SI) is likely to undergo a somewhat revolutionary change in the near future. The Consultative Committee on Units (CCU) has recommended that new definitions of the kilogram, ampere, kelvin, and mole, based on specified values of the Planck constant, the elementary charge, the Boltzmann constant, and the Avogadro constant, should be adopted. In its most recent meeting in September 2010, the CCU went a step further and drafted a new proposed definition of the entire SI based on simply specifying that a particular set of constants would have certain values when expressed in the new SI units. This is a break from the earlier concept of measurement standards based on tangible artifacts, although the new type of definition is already effectively in place for the meter. An overview of the planned redefinition and its current status will be reviewed in this talk.

460. Overview of Watt Balance Experiments to Measure the Kilogram

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This talk will summarize the latest news on the watt balance technique. The watt balance measures mechanical power in comparison to electromagnetic power, resulting in a measure of the Planck...
constant. Thus mass can be measured relative to a number of electronic references: time, length, voltage, and resistance. There are four other laboratories doing similar research, and one using a slightly different approach. The latest results from the watt balance measurements and the Avogadro counting experiments are approaching agreement, but are not yet within the 36 and 30 nW/W standard relative uncertainties of the best published results.

461. The Molar Mass of Silicon and its Relationship to the Determination of the Avogadro Constant

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An international effort aimed at a determination of the Avogadro constant by counting the atoms in a $^{28}$Si crystal has recently been completed (B. Andreas, et al., Phys. Rev. Lett. 106, 030801 (2011)). The work is relevant to the redefinition of the kilogram since such a definition will likely be based on the Planck constant, and the Avogadro constant provides an independent route to the Planck constant. The project, which began in 2004 and involved several metrology institutes from around the world, was centered on the physical and chemical characterization of a sphere of crystalline silicon highly enriched in the $^{28}$Si isotope. Measurement of imperfections, lattice parameter, surface, mass, volume, molar mass were performed to determine the Avogadro constant. The measurement of the molar mass of the Si sphere was performed at the Physikalisch-Technische Bundesanstalt (PTB) in Germany. This molar mass measurement presented significant challenges that were addressed at PTB using multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) to perform a novel modified isotope dilution method. Recently, researchers at NIST were approached by the PTB research team and asked to independently reproduce the measurement using similar instrumentation at NIST. These measurements are currently in progress at NIST. The talk will review the concepts behind the international Avogadro project, the role of the molar mass determination within the project, the measurement challenges faced, and the novel concepts developed at PTB to deal with these challenges.

Ambient Ionization Methods for Biological Mass Spectrometry
Organizer: A. Vertes

462. Laser ablation electrospray ionization (LAESI) mass spectrometry for the analysis of single cells and tissues

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Although the direct analysis of cells and tissues promises new insight on functioning biological systems, the interrogation of untreated samples has long been a challenge due to their compositional complexity and, in the case of single cells, the extremely small volume. A cell with ~20 µm diameter, corresponding to a large mammalian cell, has a volume of ~4 pL, whereas a large plant cell can have a volume of up to ~1 nL. Recent advances in the sampling and mass spectrometric analysis of such systems include laser ablation electrospray ionization (LAESI). We have shown that LAESI mass spectrometry is capable of detecting over 300 ionic species from large single cells. Identification of these species has revealed that they mostly correspond to metabolites, lipids and to abundant proteins. To facilitate finding biomarker candidates in comparative studies, we have adopted a multivariate statistical method, orthogonal projections to latent structures discriminant analysis (OPLS-DA) for LAESI mass spectrometry. The method successfully focused our search for the metabolites in cells of different phenotypes that accounted for most of the variance in the mass spectral data. We
also tested the possibility of using single cells as pixels in tissue imaging by LAESI mass spectrometry. Strong correlation was found between the distribution of cell phenotypes (pigmentation) and of secondary metabolites responsible for pigmentation supporting the idea of cell-by-cell imaging. Combining cell dissection with LAESI mass spectrometry (see figure below)

enabled the analysis of subcellular regions. Ablation of a single ~20 µm diameter nucleus of a large epidermal cell resulted in the detection of over 30 ions. More than half of these ions were assigned to primary metabolites including amino acids and carbohydrates. To gain insight into intracellular metabolic heterogeneity, metabolites from the exposed cell nucleus were compared with those from the exposed cell cytoplasm. Large differences were observed in the abundance of some metabolites, such as alliin and thymine, between the cell nucleus and the cytoplasm. Improvements in sensitivity are needed to analyze smaller cells and other subcellular compartments.

463. Development of a low power ion trap mass spectrometer for mars

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The Mars Organic Mass Analyzer (MOMA) is a low power ion trap mass spectrometer that is being developed for NASA and the European Space Agency 2018 Mars mission to provide both in situ laser desorption measurements as well as serving as a detector for gas chromatography. The instrument utilizes a low voltage (300-700V) fundamental RF and a novel supplemental frequency scanning mode to achieve a mass range up to 2000 Daltons. The instrument has also been interfaced to a gas chromatograph, using a novel internal EI source with filaments embedded into the ring electrode. The instrument has been operated with carbon dioxide (the major component of the Mars atmosphere) as a bath gas. In addition, it has been used to test alternative methods for electron emission, such as carbon nanotubes. While envisioned as an instrument for operation on a Mars Rover, it is also intended for development for homeland security and point-of-care diagnostics.


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Mass Spectrometry has recently been inundated with many new ionization sources but few of them have been carefully characterized as to the mechanisms of ionization. In MALDESI, samples are ablated using an IR or UV laser. The ablated material then interacts with an ESI plume which is co-linear with the inlet to the mass spectrometer. Our goal is to use various solvent and molecular systems to help describe the ionization mechanism of MALDESI. In an effort to increase ionization efficiency,
we have also incorporated the use of RASTIR to entrain the ESI plume into the MS inlet and to help prolong the interaction of the ablated material with the ESI plume.

An IR- or UV- laser was used to excite an added or endogenous matrix (used to facilitate analyte desorption). It was proposed that the ablated material interacts with the electrospray droplets which then undergo desolvation and fission to produce multiply-charged ions according to an ESI-like mechanism. Instrumental and geometric parameters of the source were systematically examined using a systematic design of experiments (DOE) to determine how they affect ion intensity, charge state, and signal to noise. The ionization mechanism was probed through the use of various solvent systems (deuterated and organic gradient) and molecular systems (quaternary amines, stable isotope labeled peptides, and peptides of increasing hydrophobicity). The effect of the RASTIR coupled to this source was also investigated. When investigating an ionization source, there are many instrumental and geometric variables which have the potential to affect the observed signal. To efficiently investigate the effects that these parameters have on ion intensity, charge state, and signal to noise, a series of Fractional Factorial Design Experiments (DOE) were developed using the program JMP. Quaternary amines, peptides of increasing hydrophobicity and a gradient electrospray were used to demonstrate the hydrophobic effect of desorbed analyte incorporation into the electrospray droplets. The interaction of the desorbed analyte with the ESI was investigated through the use of H/D exchange, stable isotope labeled peptides, alkylating reaction kinetics. Analytical figures of merit were then determined for different molecular classes. An Air Amplifier was coupled to the MALDESI ion source with the intention of extending the interaction between the ablated material and ESI plume.

CFDV Student Award Symposium for Separation Science
Organizer: M. Selman

465. Enantiomeric separations of cationic and anionic pharmaceutical compounds using dual opposite injection capillary zone electrophoresis with neutral cyclodextrins

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Enantiomers typically share identical physical and chemical properties while displaying drastically different biological properties. Quantification of the enantiomeric purity of pharmaceutical compounds is necessary to prevent harmful or inactive compounds from being administered along with the desired compound. The technique of dual opposite injection capillary zone electrophoresis (DOI-CZE) allows for the simultaneous, efficient separation of cations and anions. By adding a chiral selector such as a neutral cyclodextrin to the background electrolyte, cationic and anionic enantiomers of pharmaceutical compounds can be separated during the same electrophoretic run using DOI-CZE. Separations of the enantiomers of cationic pharmaceutical compounds, such as ephedrine and propanolol, and anionic pharmaceutical compounds, such as ketoprofen, have been investigated using 2-hydroxypropyl-β-cyclodextrin (HPβCD) in the DOI-CZE format. The enantiomers of propanolol were resolved at an Rs of 1.33 using a 10mM HPβCD concentration, the enantiomers of ketoprofen were resolved at an Rs of 4.27 using a 20mM HPβCD concentration, and the enantiomers of ephedrine were resolved at an Rs of 1.38 using a 120mM HPβCD concentration. Future work will involve both asynchronous and simultaneous resolution of enantiomers of other cationic and anionic pharmaceutical compounds using HPβCD in the DOI-CZE format.
466. MEKC investigation of the chiral recognition capabilities of bile salt micelles
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This work involves the systematic study of the chiral recognition capabilities of bile salt micelles using Micellar Electrokinetic Capillary Chromatography (MEKC). Chiral separations are critical for the analysis of pharmaceutical formulations and new methods of efficient chiral separation are attractive. Equally important, this MEKC work, coupled with NMR investigations of bile salt micellar media, will contribute to the fundamental understanding how bile salt micelles behave and how they can be used to perform chiral selection. This work involves elucidating some of the characteristics of the interactions between bile salts and the model chiral analytes 1-1'-binapthyl-diylhydrogenphosphate (BNDHP) and 1-1'-binaphthol (BN). Cholate and deoxycholate are bile salts that have been found to form micelles capable of chiral recognition of these model analytes. Electrophoretic mobilities (mₑ) for both the R- and S-BNDHP as well as the R- and S-BN isomers have been determined. A larger difference in mobility means better separation of the two isomers. In all cases, the S- isomer is more highly retained than the R-. Despite the structural similarities, the two isomers of BN and of BNDHP are effectively separated at different bile salt concentration. Resolution of the BNDHP isomers reaches a maximal value at 20 mM deoxycholate or 30 mM cholate; with higher concentrations resulting in lower chiral resolution. In contrast, the isomers of BN become resolved when a discretized transition takes place at about 20-30 mM for deoxycholate and about 40-50 mM for cholate. In total, these data support a multi-step bile salt micelle-formation process.

This work was supported by ACS-PRF grant 47262-B6 and NIH grant R15EB003854 from the National Institute of Biomedical Imaging and Bioengineering.

467. Optimizing a short-end electrophoretically mediated micro-analysis (EMMA) assay for creatinine
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This work involves optimization of an in-capillary reaction assay carried out in the short end of a capillary electrophoresis (CE) tube to determine the concentration of creatinine in a sample solution. CE is now a well established analytical technique and has great potential in the area of clinical analysis of bio-fluids. In this work electrophoretically mediated micro-analysis (EMMA) is used in conjunction with short end injection to improve upon the previously reported in-capillary Jaffe assay for creatinine. The goals of this work are (1) to shorten the analysis time, (2) to maximize the amount of product formed and (3) to increase the sensitivity of the assay. All experiments were performed on the short end of the capillary to minimize analysis time. The zone overlapping time, the buffer concentration and pH were systematically altered with various borate background electrolyte concentrations to maximize the reagent zone overlap and thereby maximize product formation. As borate concentrations are lowered (20-40mM) the rate of electro-osmotic flow increases and the product is not separated from the reaction zone, and these conditions are advantageous because post-separation degradation of the product is minimized. Detection at 505 nm allows the product to be selectively detected. In all, short end injection with low borate concentrations may be an attractive alternative to traditional long-end approaches. A discussion of the degradation of the Jaffe product as well as the effect of additional sodium hydroxide plugs as a third reactant for the Jaffe reaction will be presented.
Using Ferrocene For Improved LC-MS Detection of Arteriosclerotic Chlorinated Fatty Alcohols

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Molecular targets for arteriosclerosis such as chlorinated alcohols in the blood eluted by Liquid Chromatography (LC) and detected by Mass Spectrometry (MS) may be detectable before arteriosclerotic plaques.[1] Build-up of plaque leads to artery wall stiffening interfering with artery elastic recoil function. [1,2] Researchers are interested to develop innovative methods to detect, track, and analyze molecular targets linked to atherosclerotic plaques to improve diagnostic speed enabling early detection and disease prevention while observing the biological mechanisms involved in atherosclerotic plaque formation.

Research shows chlorinated fatty alcohols in the bloodstream as one molecular target that may be key to understanding the development of arteriosclerosis.[3] Reports show the detection of the 2-chlorohexadecanal (2-ClHDA) molecule in atherosclerotic tissues at concentrations 1400 fold greater than found in normal artery walls.[4] 2-ClHDA is a long chain chlorinated fatty aldehyde that is reduced in living systems to a chlorinated fatty alcohol (α-ClFOH).[5] We improve detection of the chlorinated alcohols using NN-Dicyclohexylcarbodiimide (DCC) as a reagent to convert ferrocene-carboxylic acid into a reactive acylating agent for coupling to an alcohol functional group of long chain fatty alcohols like α-ClFOH.[6,8] Overall mass is increased with a four part isotopic ratio while imparting an electro-active functional substituent creating a strong and predictable LC-MS fragmentation pattern for improved detection.[7,8] Initial results indicate that the ferrocene derivatives of fatty alcohols are 10,000 times more sensitive when detected by LC-MS than the free alcohol alone. Our work now focuses on using this method for detection of ppth alcohol concentrations.


469. Evaluation of Dual-Opposite Injection Capillary Zone Electrophoresis Using a Conventional Capillary Length and Unmodified Cartridge

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Dual-opposite injection capillary zone electrophoresis (DOI-CZE) is a method of dual sample introduction and separation in capillary electrophoresis that has no bias in resolution and analysis time that is used for the simultaneous separation of anions and cations [1]. In previous research, the cartridge of a capillary was modified to allow a longer capillary length at the outlet to improve the separation of anions traveling toward the detector from the cathodic end of the capillary. In this study, a DOI-CZE separation is achieved using a standard cartridge and capillary length. The precision of DOI-CZE separations is evaluated and compared with the precision of CZE separations using the same capillary/cartridge and DOI-CZE separations with the longer capillary in terms of migration times, resolution, and peak areas.


470. Development of a Project-based Laboratory Involving LC-MS to Introduce Students to Drug Discovery

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We have developed a multiple week laboratory project that introduces students to the critical role liquid chromatography-tandem mass spectrometry (LC-MS-MS) plays in drug discovery. This experiment combines parallel synthesis of a library of molecules with the power of LC-MS-MS to quantitatively analyze samples from complex, biological matrices.

Drug discovery is a complex process involving the synthesis and screening of large libraries of molecules. Drug development requires screening of drug candidates against a biological target, but also the analysis of the interaction of the drug candidate’s absorption, distribution, metabolism, excretion, and toxicity (ADMET) properties. Separation of drug candidates from biological matrices at μM concentrations is essential for drug discovery. Our study aims to develop a project-based undergraduate experiment that introduces students to the important role biological separations play in drug discovery through the parallel synthesis of lidocaine derivatives and evaluation of their metabolic stability using LC-MS-MS.

In the project, students create a library of derivatives of the anesthetic drug, lidocaine. Next the students develop LC-MS-MS methods to analyze their derivative and prepare a standard curve that allows them to quantify the concentration of their derivative relative to an internal standard. Finally, students incubate their lidocaine derivative with rat liver microsomes. Students analyze samples at various time points using their LC-MS-MS method to determine the rate of metabolism of the derivative.
471. Transfer of thin layer chromatography pharmaceutical product screening methods designed for use in developing countries to quantitative High Performance TLC densitometry methods

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A model for transfer of four rapid thin layer chromatography (TLC) screening methods used to detect substandard and counterfeit pharmaceutical products to quantitative high performance TLC (HPTLC)-densitometry methods will be described. These methods for acetaminophen, acetylsalicylic acid, ibuprofen, and chlorpheniramine maleate are contained in a Compendium of methods developed by A.S. Kenyon and T.P. Layloff at the U.S. Food and Drug Administration (FDA) for use in countries with limited resources. The newly developed quantitative methods use standard and sample solution preparation methods that provide a suitable standard calibration curve covering the range of 70-130% of the label value of the pharmaceutical product and bracketed sample zones; Merck high performance TLC (HPTLC) silica gel 60 F\(_{254}\) glass plates; automated standard and sample application with a CAMAG Linomat; development with the mobile phase in a CAMAG twin trough chamber; and automated densitometry at 254 nm with a CAMAG Scanner 3 for detection, identification, and quantification.

The HPTLC plates give better detection sensitivity, efficiency, selectivity, and resolution than the TLC sheets used in the original Compendium screening methods, and the new methods overcome the deficiencies in technology related to manual application and visual zone comparison that do not allow the Compendium TLC procedures to support regulatory compliance actions. The transferred methods can be fully validated according to International Conference on Harmonization (ICH) guidelines or by interlaboratory studies if their applications require. The approach described can be used to transfer the remaining Compendium methods as well as the Global Pharma Health E.V. (GPHF) Minilab kit TLC screening methods that are widely used in developing countries.

472. Capillary and Microfluidic Gradient Elution Isotachophoresis Coupled to Capillary Zone Electrophoresis for Femtomolar Amino Acid Detection Limits

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In this work, gradient elution isotachophoresis was combined with capillary zone electrophoresis (GEITP-CZE) in a single microcolumn. The multistage approach addresses the issues of analyte resolution difficulties in GEITP, as well as poor concentration sensitivity in CZE. GEITP employs rapid electrophoretic focusing at a discontinuous ionic interface within a sample well generated through combined electroosmotic and hydrodynamic flows. The interface and enriched analytes are then pulled into a capillary or microchannel as the counter-flow is reduced for on-column detection. To transform GEITP-focused samples to CZE-based separation, the sample solution is replaced with CZE buffer solution while maintaining hydrodynamic flow to ensure migration toward the detector. The single solution switch and lack of polarity inversion allows for reproducible separations (typically <6% relative standard deviation in peak heights and <0.5% in migration times). Low-pressure hydrodynamic flow during CZE allowed for flexible resolution adjustment, with a linear increase versus the square root of migration time, without altering the separation column, field strength, or electrolyte system. As a first demonstration of the applicability of GEITP-CZE, a series of amino acids to be assayed for in future Mars exploration missions as indicators of biological life were studied. Separation of six amino acids, with limits of detection as low as 200 fM, were achieved using a capillary format with a total analysis time of 11 min. A glass-based microfluidic implementation is also demonstrated that can perform GEITP-CZE in 1 cm effective lengths.
473. Non-Invasive Spectral Imaging for Characterization of Cultural Heritage Materials


Originally developed for remote sensing, astronomical imaging, remote sensing, and optical character recognition, spectral imaging tools have been adapted for application to cultural heritage materials to enable the non-invasive chemical characterization of these historic documents and objects, recover data from historical texts on degraded manuscripts, and monitor non-visible changes in fragile materials to optimize conditions for storage and display of cultural heritage. An ongoing challenge associated with the preservation of cultural heritage is this need for advances in non-invasive, non-destructive analytical techniques that can be used to identify and analyze substrates (paper, parchment) and media (inks, pigments, colorants). A range of case studies will be utilized to discuss the challenges associated with characterizing cultural heritage materials. These will include maps, historic manuscripts in US history, and representative manuscripts from other cultures. Studies of Portolan Charts, L’Enfant Plan of Washington D.C., Jefferson’s handwritten draft of the Declaration of Independence, the Waldseemüller 1507 World Map, Herblock drawings and other objects to illustrate characterization of colorants and substrates, in addition to detection of non-visible changes due to exhibition and storage environmental conditions. The adaptation of spectral imaging systems as a tool for non-contact characterization of cultural heritage allows the collection of chemical identification information about materials without sampling, a critical consideration for cultural heritage materials. The Library of Congress has been developing the application of hyperspectral imaging to the preservation and analysis of cultural heritage materials as a powerful, non-contact technique. It allows non-invasive characterization of materials, by identifying and characterizing colorants, inks and substrates with narrow band illumination to protect the object, while also monitoring deterioration or changes due to exhibit and other environmental conditions. Contiguous illumination from the ultra-violet, visible and infrared spectral regions allows the capture of lost, obscured and deteriorated information. The resulting image cube allows greater capabilities for mapping and coordinating a range of complementary chemical and spectral analyses. This image cube creates a new “digital cultural object” that is related to, but recognized as a distinct entity from the original. The range of data this object contains encourages multidisciplinary collaboration for the integration of preservation and cultural information. The integrated hyperspectral camera, lighting system and data acquisition process allows the creation of a standardized capability to collect high resolution images for sophisticated image analysis and processing, the image cube created enabling the specific x,y,z and 3D spectral curves unique for each material. Integrating imaging with material characterization supports the development of spectral preservation databases and spatial mapping to enhance the tracking of deterioration changes. The development of this non-destructive analytical technique advances the examination of nationally and internationally significant cultural heritage objects. The integration of data from other analytical techniques creates a full analytical mapping of objects for non-destructive analyses of a variety of heritage materials, including manuscripts, maps and early photographs. The imaging program includes the development of a spectral reference database, and the integration of data from other non-invasive analytical techniques, to create a full analytical mapping of objects for non-destructive analyses of collection materials.
474. Details of Mimbres Pottery Production and Distribution Revealed by INAA

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Gilman et al. (1994)[1] published the results of the first chemical-based provenance study of Mimbres pottery. Using instrumental neutron activation analysis (INAA) to chemically characterize ca. 120 ceramic specimens, researchers identified six compositional groups indicative of multiple production locales, including one group attributed to the Powers Ranch site in Arizona. The 1994 study effectively served to debunk the idea that Mimbres pottery only was produced in the Mimbres Valley and immediately adjacent areas. In the ensuing years since publication of Gilman et al.’s seminal study, ca. 3800 Mimbres, Jornada, and related pottery specimens and clay samples representing dozens of projects have been analyzed at the University of Missouri and Texas A&M. Although these subsequent studies confirmed the patterns reported by Gilman et al. (1994) and produced evidence for local ceramic production at a number of sites in the Mimbres Valley and elsewhere, there has been no synthesis of the data. Additionally, every INAA study of Mimbres pottery that occurred since 1994 has failed to consider all (or even most) extant data which has resulted in conflicting views regarding Mimbres pottery production and distribution. An ongoing major analytical effort focused on all extant INAA data has resulted in the identification of at least 45 Mimbres, Jornada, and related compositional groups. Mimbres groups are attributable to production locales in the Rio Grande, Mimbres, and Gila drainages as well as in various parts of the Deming Plain. It is apparent that most sites produced pottery that was distributed in vast quantities across the landscape which has hampered efforts to identify production locales. This paper provides an overview of our results and interpretations to date.


475. Archaeological approach to the analysis of cultural heritage in library collections

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The primary goal of conservators of cultural heritage collections is to preserve. Conservation treatment of collection items is often an essential means toward that end. As conservators and cultural heritage scientists are well aware, interventions that are designed to alter physical and chemical properties in order to enhance longevity and access may inadvertently obscure inherent material evidence. As the advent of more sensitive and convenient analytical techniques allows us to access relatively larger amounts of this historical material information, we should consider anew the value of taking a more archaeological approach to all cultural heritage materials, regardless of whether they were dug out of the ground, lost in a drawer, or housed in a library for a significant part of their existence. In this view, we should devote greater resources to capturing detailed material evidence before treatment as part of standard documentation practice in order to glean information pertaining to an object’s “life,” from manufacture through treatment history to current condition. The empirical and analytical information gained is valuable as the basis for research into degradation and behavior of important historic materials.

For example, iron gall inks were the major writing medium from the Middle Ages through the 19th Century in the Middle East and Europe, and are present in hundreds of thousands of important cultural heritage objects worldwide, including books, manuscripts and artistic drawings. This type of ink, which was manufactured from a great variety of recipes based on iron salts and gall nuts, is well
known to present severe preservation problems, especially in library and archival collections: the ink may strike through paper and can even appear to burn holes; paper surrounding the ink may become brown and brittle; cracks and losses may occur. Inks that exhibit signs of this deterioration are typically treated by methods that involve washing and often chemical chelation. However, while wet treatment and introduction of complexing agents may extend the life of cultural heritage containing these inks, treatment can also cause the loss or obscuring of information that pertains to provenance and authenticity, as well as the history of technology in different regions of the world. Selected evidence of changes induced to iron gall ink before and after different treatments, as determined by techniques such as X-ray photoelectron and X-ray fluorescence spectroscopy, will be presented and discussed in the context of what material evidence from historic inks may tell us about certain historical documents and manuscripts.

476. Spectroscopic and chromatographic analysis of mixed media artists’ paints

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Frequently conservation scientists are asked to analyze paint media to assist with a conservation treatment or identify a deterioration phenomenon. Often the question is presented in an either-or format: is this acrylic or alkyd? Is this oil or tempera? However an artist prone to experimenting may not have chosen to use only one paint medium. Scientists at the Smithsonian Institution have begun testing the limits of their standard laboratory protocols when examining mixtures of modern paint media: alkyds, acrylics and oils. Although infrared identification of a single binding medium is straightforward, mixtures of paints, with contributions from pigments and fillers, as well as the effects of aging can complicate interpretation of the infrared spectrum.

When looking at mixtures of modern acrylic, alkyd and oil paints, infrared spectroscopy was frequently able to identify one component in mixed media samples, but it did not always identify the most prominent binding medium in the mixture. Py-GC-MS is also easily able to identify a single binding medium, but relies on multiple analyses to conclusively identify all the elements in mixed media paint. A new laboratory protocol is being developed to allow both conservation scientist and conservator more confidence in determining what components are present in mixed media paints.

477. Rheological effects of addition of organic solvents to hydrogels with partially hydrolyzed poly(vinyl acetate)-borate networks: Potential applications to cleaning painted surfaces

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Thickening agents are commonly used during art conservation treatments to reduce evaporation and lateral spreading of solvent. They also allow solvents to be placed in defined areas and on vertical surfaces without flow.1 We report here the preparation of transparent ‘hydrogels’ of partially hydrolyzed poly(vinyl acetate)s cross-linked by borate ions (PVAc-B) containing up to 75% of a polar organic solvent (such as methanol, ethanol, 1- and 2-propanol, acetone, N-methyl-2-pyrrolidone, or methyl ethyl ketone) in the liquid component. The highly labile cross-links result in dynamic networks, making the PVAc-B malleable and self-healing, two desirable properties for cleaning agents.2

The concentrations of PVAc-B-derived residues left on painted surfaces with acrylic and aged natural varnish after cleaning have been determined spectrofluorimetrically using gels with fluorescein covalently bound to the PVAc-B. The tests detect no polymer residues after cleaning treatment (detec-
tion limit $\sim 0.14 \mu g/mm^2$). Fluorescence studies also show that solvent is contained in the immediate surface area defined by the gel.

Rheological studies demonstrate that the PVAc-B have viscoelastic networks but are not true gels – the storage and loss moduli cross at specific frequencies. The elasticity of the PVAc-B can be increased drastically upon incorporation of organic solvents. Addition of an organic solvent to the liquid component increases the fraction of the borate ions participating in cross-links and reduces the free water content – the solvent acts as a structure maker for water in the systems. The gel networks are sensitive to the molecular weight of the polymer. By probing systematically the variables that affect the formation and stability of these materials, new systems for the cleaning of a variety of surfaces have been tailored specifically for the field of cultural heritage conservation. The PVAc-B system has been used to remove a discolored and soiled coating from an early 20th century painting.

As shown clockwise from the top left panel below: a magnified image of the surface before cleaning; the same area covered by a 30/70 acetone/water gel; the surface after gel removal; and the surface (cleaned) after a second gel application and clearing.

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**Food Safety**

Organizers: K. Morehouse, B. Yakes

**478. Alternative Food Safety Intervention Technologies**

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Alternative nonthermal and thermal food safety interventions are gaining acceptance by the food processing industry and consumers. These technologies include high pressure processing, ultraviolet and pulsed light, ionizing radiation, pulsed and radiofrequency electric fields, cold atmospheric plasma, GRAS antimicrobials, flash pasteurization, and many others. Many of these technologies have been the focus of research at USDA Eastern Regional Research Center. The results of our research, including applications which have been transferred to the food processing industry, will be discussed.
479. Evolution of compendial testing standards for food ingredients to guard against economically motivated adulteration

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Economically motivated adulteration (EMA) presents a persistent and significant challenge in the marketplace. Like all adulteration, EMA disrupts the integrity of any supply chain and creates unknown risks for the safety of the food (ingredients and finished products) as it traverses the supply and distribution chains and ultimately reaches the consumer. Analytical methods to detect EMA are often focused on verifying the absence of known adulterants, a strategy that is not effective for discovering unknown adulterants. The compendial testing strategy is a practical tool for guarding against both unknown and known adulterants by comprehensively evaluating the authenticity, identity, and purity of the desired ingredient(s), but is challenged by the need for methods that are both highly specific and practical for routine analysis. This presentation will report on the technical challenges and opportunities for advancing analytical science to support the compendial testing standards, including the emergence of non-targeted analytical methods and the use of chemometrics. It will also report on an on-going research project being led by US Pharmacopeia to develop new compendial analytical methods for skim milk powder to guard against EMA in the food supply.

480. Analysis of organic acids in fruit juices by liquid chromatography - mass spectrometry: An enhanced tool for authenticity testing

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Organic acid analysis plays a fundamental role in the testing of authenticity of fruit juices. Analytical methods used routinely for organic acids suffer from poor reproducibility, often give false positives/negatives for tartaric acid, and do not offer the possibility of analyte confirmation. There are conflicting reports in the literature on the presence/absence of tartaric acid in pomegranate juice, a potential indicator of adulteration with grape juice. In this work, a method based on stable isotope dilution liquid chromatography-tandem mass spectrometry is described for citric, malic, quinic, and tartaric acid in fruit juices. Validation data including precision and recovery in six types of juice are presented. Tartaric and quinic acids were confirmed in pomegranate juice at concentrations of 1-5 and ~1 mg/L, respectively. These concentrations are much lower than those resulting from adulteration with grape juice and apple juice, respectively, at the 5% level. A separate method for isocitric acid in orange juice based on the single standard addition method is also described.

481. Chemometric Analysis of Mass Spectral Fingerprints for Authentication and Quality Assessment of Scutellaria lateriflora and Dietary Supplements

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Scutellaria lateriflora, commonly known as skullcap, is used as an ingredient in numerous herbal products. However, it has been occasionally adulterated/contaminated with Teucrium canadense (TCA) and/or Teucrium chamaedrys (TCH), commonly known as germander, which contain hepatotoxic diterpenes due to the morphological similarities between the two genera. Analytical methodologies to distinguish authentic S. lateriflora from Teucrium species is needed to ensure public safety. In this study, a flow-injection ESI-MS method was used to generate mass spectral fingerprints of extracts from S. lateriflora, germander, and S. lateriflora based dietary supplement samples in 90 seconds for each sample. Chemometric analysis was used to process the mass spectral fingerprints. The newly developed method offered a fast and easy way to differentiate between the skullcap and...
germander samples and to assess the quality of *S. lateriflora* based dietary supplements sold in the US. The method successfully distinguished *S. lateriflora* (SL) from germanders (TCA & TCH) and did an excellent job of classifying *S. lateriflora* based dietary supplements sold in US.

482. Determination of carbon black in food products

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Color additives in foods, human and veterinary drugs, cosmetic products, and medical devices are regulated by the U.S. Food and Drug Administration (FDA). These dyes and pigments must be pre-approved and listed in the U.S. Code of Federal Regulations before they may be used in FDA-regulated products. Some listed color additives also are required to be batch certified by FDA prior to use. The FDA District laboratories need analytical methods for identifying permitted and non-permitted color additives in imported and domestic products in order to enforce the color additive requirements. Carbon black is a non-permitted color additive in foods marketed in the U.S. but is permitted for this use in other countries, including the E.U. The pigment, also known as vegetable carbon and carbon ash, is certifiable as D&C Black No. 2 for use in cosmetics. It is insoluble in most solvents, which presents a challenge for determining its presence in any products. We have recently developed a method for extracting carbon black from various food products labeled with or suspected to contain the color additive, by breaking down samples with nitric acid. The solutions are then filtered under vacuum and any carbon black remains on the filter. Raman spectroscopy is used to confirm the presence of carbon black.
483. **Two new methods for the detection of under-pasteurized dairy products**

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With the constant risk of foodborne illness faced by consumers; faster, more accurate and precise methods are needed to detect under-pasteurized dairy products. Existing methods for analyzing dairy samples for proper pasteurization have problems with reproducibility and accuracy, are hampered by long analysis times, and exposure of the analyst to hazardous chemicals. In order to overcome these issues, two new methods have been developed by the FDA using fluorogenic substrates for two different marker enzymes, alkaline phosphatase (ALP) and gamma glutamyl transferase (GGT). Up to twenty four samples can be analyzed on a 96-well plate. For milk, the total time to prepare the samples, analyze them by both methods is less than a half hour. Both assays have coefficient of variance of less than 5% compared to 20-70% for existing methods. The correlation between the two assays is greater than 0.999. In addition, the GGT method is more sensitive for the detection of under-pasteurization than ALP for dairy products that have been made from cooked but not pasteurized milk.

484. **Surface plasmon resonance biosensors for enhancing food safety**

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Advances in foodborne pathogen and contaminant detection continue to occur as new technology is developed or adapted for food matrices. One such technique, surface plasmon resonance (SPR) biosensor, has been applied to the detection of bacteria, proteins, drug residues, and vitamins over the last decade. In addition, SPR biosensors are beginning to address detection needs for viruses and small molecular weight toxins. These label-free, real-time biosensors are able to provide sensitive, quantitative results with rapid (<10 min) analysis times. Furthermore, SPR assays are free of the ethical and performance related concerns associated with animal bioassays and do not use radiolabeled materials that are employed in receptor binding assays.

This presentation will give an introduction to SPR technology and an overview of the advantages this method can offer. To elucidate these attributes, two marine toxin projects will be highlighted. First, our research on tetrodotoxin will demonstrate SPR biosensor performance in complex matrices and serve as a comparison of SPR results to other analytical methods. Then our research on paralytic shellfish poisoning toxins will emphasize the use of SPR sensors as an antibody screening technique. Results from this work are contributing to the improved development of both SPR assays and lateral flow immunochromatographic assays.
485. Multifunctional metal oxide–carbon nanoarchitected electrodes for aqueous asymmetric electrochemical capacitors

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Carbon fiber-paper-supported carbon nanofoams are ideal platforms for electrode architectures due to such inherent attributes as high specific surface area (300–600 cm² g⁻¹), high electronic conductivity (20–40 S cm⁻¹), and a size-tunable through-connected pore network (tens of nanometers to micrometers). The carbon fiber paper serves as a scaffold for the ultraporous carbon nanofoam, making scalability in length and width (~100 cm²) as well as thickness (70–300 µm) trivial. We have developed simple, scalable, low-cost electroless deposition protocols to introduce conformal, nanoscale coatings of metal oxides which augment the moderate charge-storage capacity of the carbon nanofoam. For example, exposing the carbon nanofoam to aqueous potassium ferrate or sodium permanganate generates nanoscale iron oxide (FeOₓ) or manganese oxide (MnOₓ) coatings, respectively, increasing the charge-storage capacity of the carbon nanofoam 2-to-10 fold without significantly affecting its high-rate capabilities. Prototype aqueous asymmetric electrochemical capacitors with these metal oxide-carbon nanofoam electrodes support operating voltages approaching 2 V, resulting in cell-level specific capacitance >30 Fg⁻¹ and an energy density of 13.5 Whkg⁻¹ within a 10-s charge–discharge timeframe.

486. Ionic liquid-based electrolytes for lithium batteries: Linking structure with electrolyte properties

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Ionic liquids have garnered considerable attention as a new class of electrolyte materials, but little is known about the link between structure, ionic interactions and electrolyte properties. It is the combination of specific attractive properties for select ILs – wide liquid range (i.e., -80°C to 250°C or higher), high electrochemical stability and conductivity, negligible volatility/flammability, etc. – that has sparked this tremendous interest. ILs incorporated into electrolytes can dramatically improve
the safety characteristics of batteries, as well as possibly increase the battery operating temperature range and enable the use of high-voltage electrodes. Little is known, however, about how the ions interact within ionic liquid-lithium salt mixtures and how this impacts electrolyte properties such as crystallization temperature, conductivity, etc. The phase behavior and ionic interactions of binary ionic liquid-lithium salt mixtures and ternary mixtures with solvents and the link between the structural interactions and electrolyte properties will be discussed.

487. Safer high voltage polymer electrolyte for lithium batteries

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The next generation of high voltage lithium battery systems is dependent upon the development of more stable electrolytes. Polymer-based systems have the required stability, but have as of yet been unable to gain widespread usage because of performance limitations. Additives based upon sulfur ionic liquid (IL) chemistries have been explored to elevate the conductivity of the electrolyte while still maintaining the wide electrochemical stability of poly(ethylene oxide) systems. The synthesized ILs are blended with a lithium salt in lithium conducting polymer matrices to produce solid electrolytes. The hybrid electrolyte has demonstrated functional ionic conductivity at 0°C, and at slightly elevated temperature ionic conductivity is on the order of 10 mS/cm. The hybrid electrolyte has demonstrated reversible stability against metallic lithium at the anodic interface and stability approaching 5 V at the cathodic interface. Development of this electrolyte presents advancement of lithium battery technology while improving safety.

488. Electrolyte in support of 5-volt lithium ion battery systems

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Li ion chemistry is established upon reversible intercalation/de-intercalation of Li+ into/from host compounds. The voltage of such an electrochemical device is determined by the chemical natures of anode and cathode, where Li+ is accommodated or released at low potentials in the former, and high potentials in the latter. The reversibility of the cell chemistry and the resultant energy density appear to be limited by the stability of the electrolyte to withstand the reductive and oxidative potentials of these electrodes. In today’s market majority of Li-ion batteries use organic carbonate as electrolyte solvents, which decompose oxidatively above 4.5 V vs. Li, and set an upper limit to the candidate cathode chemistry.
In order to formulate an electrolyte composition that supports 5.0 V Li ion intercalation chemistry, which is made available from such cathodes as LiCoPO$_4$ (~5.1 V) and LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (~4.7 V), we have explored various approaches to expand the electrochemical stability window by tailoring a high-voltage tolerant interphase through the use of functional additives and co-solvents designed/synthesized to serve as sacrificial components on those highly oxidizing cathode surfaces. Preliminary improvements with a phosphate ester additive were made in terms of building a less resistive interphase as well as retaining higher capacity during long term cycling on both LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinel and LiCoPO$_4$ cathodes. This additive also proved effective in protecting graphite from persistent exfoliation from propylene carbonate, a unique result.

Based on the surface analysis, which confirms the novel interphasial chemistry resulted from those new co-solvents and additives, we attempted to understand on a fundamental level what guides the formation of interphase on cathode surfaces. This article summarizes our recent results obtained in this research direction.
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