



# Eastern Analytical Symposium September Virtual Student Symposium

September 14, 2020

## Sessions

*Opening Remarks* – 10:00 am

*Mass Spectrometry* – 10:05 am

*Microscopy* – 11:20 am

*Spectroscopy I* – 11:45 pm

*Lunch* – 12:05 pm

*Spectroscopy II* – 1:00 pm

*Computation* – 1:50 pm

*Chromatography* – 2:40 pm

*Networking Hour* – 4:15 pm

## *Mass Spectrometry*

10:05 am

### “Acceleration of Reaction in Droplets Studied by Droplet Assisted Ionization Mass Spectrometry”

**Yao Zhang, Murray Johnston**  
University of Delaware

Droplet Assisted Ionization (DAI) is a relatively new method for online analysis of aerosol droplets that enables measurement of the rate of an aerosol reaction. It is an inlet ionization method, where ions are formed when droplets pass through a temperature-controlled capillary inlet to a mass spectrometer. Here, we used DAI to study the reaction of carbonyl functionalities with Girard's T (GT) reagent. Varying the droplet transit time between the atomizer and mass spectrometer allowed the reaction rate constant to be determined, which was found to be 4 orders of magnitude faster than what would be expected from bulk solution kinetics. Mechanisms of reaction acceleration on the droplet were investigated by varying DAI conditions including: i) increasing temperature applied on the capillary inlet, ii) decreasing the relative humidity of the air surrounding the droplets in between the atomizer and the mass spectrometer, and iii) varying the size of the droplets. It was found that the product formation was enhanced by heating the capillary inlet and decreasing the relative humidity of the air, suggesting that removing water from the droplets increased the reaction rate. Decreasing the droplet diameter increases the surface to volume ratio and can distinguish reaction on the particle surface from that in the bulk volume. The results suggest that reaction on the droplet surface plays an important role to increase the reaction rate in droplets relative to bulk solution.

10:30 am

## “Formation of Carbamate Anions by the Gas-Phase Reaction of Carboxamide Anions Derived from Capsaicinoids with CO<sub>2</sub>”

**Annie Wang, Zhaoyu Zheng, Athula B. Attygalle**  
University of Rochester

Novel chemical reactions that consume CO<sub>2</sub> as a reactant are widely sought through research today because increasing levels of CO<sub>2</sub> in the atmosphere is the cause to many environmental problems. One known reaction is the CO<sub>2</sub> addition reaction, which can be used as a diagnostic structural probe for gaseous anions under mass spectrometric conditions. We experimented with capsaicinoids, the active ingredients in chili peppers that contribute to the pungency. Daughter scan experiments on all deprotonated capsaicinoids were conducted either in ion mobility mode with mobility cell filled with CO<sub>2</sub> or ToF mode without CO<sub>2</sub> in the mobility cell. We found that upon activation, all capsaicinoids lose a 136-Da 2-methoxy-p-quinone methide unit to generate a carboxamide anion. The presence of the hydroxyl group at the para position of the vanillamine moiety is crucial for this specific fragmentation to take place. To verify the role of the hydroxyl group attached to the para position in the fragmentation mechanism, we further experimented with N-4-hydroxybenzylbutyramide and N-benzylbutyramide. We found that upon activation, the anion of N-4-hydroxybenzylbutyramide lose a 106-Da fragment for p-quinone-methide to form a carboxamide (m/z 86) which readily react with CO<sub>2</sub> to generate a carbamate ion (m/z 130). In stark contrast, the anion from N-benzylbutyramide did not form a CO<sub>2</sub> adduct because for the initial p-quinone-methide elimination, the participation of the para hydroxy group is necessary. Thus, we report that for the CO<sub>2</sub> adduct formation, a hydroxyl group must be at the para position of the benzene ring bearing the -CH<sub>2</sub>-NH-COR moiety.

10:55 am

“Solid Phase Micro-Extraction (SPME) to Determine Volatile Organic Compound (VOC) Mixing Ratio in Atmospheric Flow Tube Studies”

**Devon N. Haugh**, Devan E. Kerecman, Issak Proaño, Michael Apsokardu, Murray V. Johnston  
University of Delaware

In the atmosphere, volatile organic compounds (VOCs) participate in gas phase chemical reactions and contribute to growth of secondary organic aerosol (SOA). Since SOA contributes to atmospheric albedo, and therefore, cooling, its growth processes must be thoroughly studied. Many laboratory studies use reaction chambers, like a flow tube, which combine gas phase reactants such as VOCs and ozone. Then, modeling these experimental results can allow for predictions about future climate. The reliability of these studies, however, comes from their ability to accurately determine mixing ratios of starting reactants. Here, we have used solid phase micro-extraction (SPME) and gas-chromatography mass spectrometry (GC-MS) to quantitatively determine the gas phase concentration of the VOC reactant used in flow tube studies,  $\alpha$ -pinene. Gas phase  $\alpha$ -pinene was sampled from the flow tube inlet flow using a fused silica SPME fiber for varying lengths of time. Then, the fiber was injected into the inlet of a Waters GCT Premier Mass Spectrometer where the intensity of the signal from  $m/z$  93, which corresponds to the  $\alpha$ -pinene base peak, was compared to that of several standard solutions to determine the amount of  $\alpha$ -pinene sampled onto the SPME fiber, and therefore the gas phase mixing ratio, based on the diffusion properties of the fiber and flow parameters of the inlet.

## *Microscopy*

11:20 am

“Inorganic Quantitative Analysis Experiments through Digital Microscopy Detection of Precipitates”

**Catherine Amoateng, Krista Wilson, Ellen Yeziarski, Hang Ren, Andre' Sommer and Neil Danielson**  
Miami University

An inorganic qualitative analysis experiment has been part of the first-year chemistry laboratory course sequence for many decades but has never been updated for low level quantitative detection of cations and anions. Recently the use of a fabricated elastomer lens in conjunction with a smartphone and image analysis has permitted low ppm detection of lead (II) as the chromate precipitate. In the present investigation, we have used an inexpensive digital microscope to generate images of dried precipitates of  $\text{PbCrO}_4$  originating from micro-liter droplets of aqueous solution. Quantitative information is then extracted at the low ppm level using Image-J open source software available from the National Institutes of Health (NIH). The student experiment will focus on the determination of zinc in supplements using ferrocyanide precipitation chemistry and this designed microscopic imaging technique. Students will gain knowledge to explain the formation and detection of microscale precipitates using solubility constant calculations ( $K_{sp}$ ) and image analysis. We envision the digital microscopic imaging method to have broad incorporation into physical and analytical chemistry laboratory courses as well as the first-year lab.

## *Spectroscopy I*

11:45 am

### “Probing the Acidity and Basicity of Thermally Activated Zirconium Metal-Organic Frameworks”

**Ryan McDonnell**, Venkata Swaroopa Datta Devulapalli, Tian-Yi Luo, Matheus L. De Souza, Nathaniel L. Rosi, Eric Borguet  
Temple University

Metal-organic frameworks (MOFs) are 3D porous materials and hosts of acidic and basic sites which can promote catalysis, e.g. degradation of toxic chemicals.

Optimization of such applications of MOFs would benefit from a fundamental understanding of the presence and relative acidity/basicity of these sites. Studying the effects of thermal activation on UiO-67-X (X: -H, -NH<sub>2</sub>), a 12-connected zirconium metal organic framework, Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(COO)<sub>12</sub>X, and its interactions with acidic and basic probe molecules gives insight into the type, quantity and strength of basic and acidic sites on these MOFs respectively. We hypothesize that successive thermal activations lead to structural changes, including defect formation, which induce additional Lewis acidic and basic sites. Herein, we study and compare the adsorption of two probe molecules, CD<sub>3</sub>CN and CHCl<sub>3</sub>, on thermally activated (423 – 623 K, in 50 K intervals) MOFs. Using temperature programmed desorption mass spectrometry (TPD-MS), the distribution and strength of binding sites for probes are compared. Using in-situ Fourier transform infrared spectroscopy (FT-IR) and temperature programmed infrared (TP-IR), the interactions of CD<sub>3</sub>CN and CHCl<sub>3</sub> with MOFs are identified upon adsorption and during desorption. The results show that the binding energies of CHCl<sub>3</sub> adsorbed on UiO-67 activated to successively higher temperatures remain similar in value, implying no impact of thermal activation on the strength of basic sites of UiO-67 MOFs. Irreversible hydrogen bonding is observed between CHCl<sub>3</sub> and MOF, but the IR reveals reversible hydrogen bonding between CD<sub>3</sub>CN and MOF.

## *Spectroscopy II*

1:00 pm

“Spectral analysis with a smartphone: Evaluation for qualitative analysis of spices”

**Caitlin Kurey, Mary Lynn Grayeski**  
Marywood University

Analytical figures of merit are evaluated for potential spectrophotometric qualitative analysis using a commercial smartphone app, Color Analysis Pro. With the trend toward miniaturization of chemical measurements and on-site analysis, investigations of the potential of smartphones as a spectrophotometric tool have emerged. Advances in technology have produced devices with high resolution cameras and high-performance computing power. However, most reported applications require additional hardware and sensors. We posed the question: “Are commercial color analysis apps capable of qualitative analysis?” The app, Color Analysis Pro, reports colors as quantifications of the primary colors, enabling the comparison of images based on the spectrum of the recorded picture. Because our lab is also interested in chemical education, an application that might be suitable for elementary school students studying light was selected for the study. “Color profiles” of a variety of similarly colored spices (turmeric, cumin, cinnamon, garam marsala, cloves, curry and coriander) were recorded and compared for uniqueness of their “spectra.” The profiles were indeed unique based on primary colors identified and quantified by the app. Data acquisition, interpretation, precision, and selectivity of the method will be discussed.

1:25 pm

“Raman Microscopy Investigation of the Influence of Inter-Leaflet Lipid Translocation on Multivalent Protein Capture at Supported-Lipid Bilayers”

**Grant J. Myres, Jay P. Kitt, Eric M. Peterson and Joel M. Harris**  
University of Utah

Binding of multivalent proteins to ligands at supported lipid bilayers is often exploited in the development of biosensors. Previous studies have indicated that mobility and surface density of ligands attached to lipid interfaces are crucial in enabling protein binding to multiple ligands. A potentially overlooked consequence of working with supported lipid bilayers is the impact of inter-leaflet lipid translocation on ligand density and accessibility. In this work, we use confocal-Raman microscopy to characterize IgG monoclonal mouse anti-biotin binding to biotin-capped lipids in bilayers supported on the surfaces of porous silica. The impact of lipid translocation between bilayer leaflets was investigated by comparing IgG binding at fluid-phase POPC and gel-phase DPPC bilayers prepared with equal fractions of biotin-capped lipid. DPPC bilayers were observed to have ~50% less IgG capture compared to fluid-phase POPC, indicating translocation of the biotin-capped lipids in POPC bilayers likely contributes to a doubling of available biotin ligands. To test whether inhibition of lipid-translocation explains the smaller IgG capture on gel-phase DPPC bilayers, protein capture was performed on a DPPC monolayer assembled on a nitrile surface consisting of a single solution-accessible leaflet. The protein surface coverage observed on a DPPC monolayer was found to be equivalent to that on a DPPC bilayer, indicating that bilayer translocation in gel-phase DPPC is inhibited unlike in the fluid-phase POPC bilayer. Accounting for lipid translocation, the dependence of captured protein versus ligand density (0-5 mol%) on POPC bilayers showed a constant 1:2 protein binding valency until protein surface saturation.

## *Computation*

1:50 pm

### “Multivariate Analysis of Textile Dyes”

**Gabrielle Feldman, Caelin Celani, Karl Booksh, Jocelyn  
Alcantara-Garcia**  
Washington & Jefferson College

Fiber Optic Reflectance Spectroscopy (FORS) shows a promising way to detect chemical species within artwork and textiles nondestructively. High Performance Liquid Chromatography (HPLC) is commonly used and has a database but is destructive. A series of 120 spectra across 20 textile samples were collected by sampling two spots on each sample, with 3 spectra taken at those points. Using multivariate statistical analysis, data from the sampled textiles in the Norwich Book were used to create mathematical models that would classify samples based on similar chromophore combinations. To these ends, Principal Component Analysis, K-Means Clustering, Hierarchical Clustering, Fuzzy Clustering, and Model Based Clustering were applied to the data, which indicated the presence of 3-4 distinct groups. This work can then be compared to and/or combined with HPLC data to establish a database for FORS spectra of chromophores that can eventually be used to classify future textile samples of interest. Future work will include finishing validation for ideal number of clusters, comparing spectroscopic data to HPLC data, and using classes found in cluster analysis for classification methods.

2:15 pm

## “DFT Investigations of Charge-Transfer Cofactors in Photosynthesis”

**Amanda Malnati**  
Smith College

Energy demands continue to grow as we depleted our fossil fuel resources and damage the global environment. The world is in need of affordable and efficient renewable energy, so we turn to nature to provide a blueprint. Photosynthesis performs highly efficient solar energy conversion and our goal is to understand and replicate its design principles. Quinones play an important role in charge-transfer during photosynthesis. The two quinones in photosystem II (PSII), the primary and secondary plastoquinone, QA and QB, have identical chemical structures but perform different functions. In this study we use computational methods to better understand the functional tuning of the QA cofactor in PSII. We use the software program, ORCA 4.0, to run Density Functional Theory (DFT) calculations. We studied five benzoquinone derivatives as neutral molecules, anionic molecules, anionic molecules in an aprotic solvent (DMSO), anionic molecules in a protic solvent (IPA), anionic molecules in protic solvent with explicit hydrogen bonding interactions to build up to complex models. The hyperfine coupling parameters and g-tensors of solvent models were calculated for comparison with experiments performed by Chatterjee et al. 2011 and Weyers et al. 2009. We then studied the HOMO/LUMO energies and eigenvalues. Our models closely matched the components of the experimental g-tensors and were in the range of the experimental Aiso values. Including explicit hydrogen bonds to the solvent IPA yields more accurate results than the implicit model confirming that there are explicit donor-acceptor interactions with the hydrogens in IPA that are “tuning” the molecule’s function.

## *Chromatography*

2:40 pm

### “Chemical Analysis of Off Taste in Wine”

**Anthony Oliphant, Dr. Shirley Fischer-Drowos**  
Widener University

Wine is a complex pool of chemical reactions that can be affected by many factors based on the environment that it is kept in. Exposure to light, air and especially time can affect wine in favorable and unfavorable ways. A coupled gas chromatograph/mass spectrometer was used to analyze the compounds present in wines of varying types covering a wide span of years. The most valuable comparisons for analyzing the effects of aging was obtained by analyzing the same brand and type of wine that was available from different years. The comparison of a 2006 and 2019 Pinot Grigio, both by SPME extraction of the liquid and head space, showed very interesting differences that correlate to sensory evaluation. Knowledge of what affects wine’s aging can allow for producers of wine to better store and predict the proper shelf and/or barrel life of certain wines, as well as identify the species that may affect the flavor.

3:05 pm

“Dimethyl carbonate as a green mobile phase in hydrophilic interaction liquid chromatography”

**Philip D. Boes, Neil D. Danielson**  
Miami University

Dimethyl carbonate (DMC) has potential as a green chemistry replacement for acetonitrile (MeCN) in liquid chromatography. We studied the use of DMC in hydrophilic liquid interaction chromatography (HILIC). The UV cutoff for DMC was measured to be near 215nm, and we have confirmed chromatographically this wavelength is usable. Because DMC has limited (13%) solubility in water, the solvent system was three component with DMC as the weak organic phase with a mixture of ethanol and water containing 10mM ammonium acetate buffer. The pH of the acetate buffer is kept at pH 6.0 in the aqueous portion which is mixed in a ratio of 1:2 (v/v) with ethanol. Using a 50mm x 4.6mm, 2.6 $\mu$ m bare silica column, this mobile phase system was examined to separate a mixture of trans-ferulic acid, syringic acid and vanillic acid. The separations were compared between MeCN and DMC as the organic portion of the mobile phase at the percentage range from 82 – 95%. We have been able to observe a modest increase in retention for DMC when compared to MeCN, with only a moderate reduction in plate counts and a slight increase in pressure, 310 PSI with MeCN vs 537 PSI with DMC at 80% organic. These trends confirm the surface tension of DMC (26.6 dyn/cm) being lower than that of MeCN (29.3) and higher viscosity of DMC (0.611 cp) as compared to MeCN (0.34). An examination of the separation of different hydroxy benzoic acids is being investigated.

3:30 pm

**“Removal of Perfluorooctanoic Acid (PFOA) in Water by a Novel Fluorinated Hydrocarbon Amine Weak Anion Exchange Resin”**

**Charles Xie, Abigail Smith, Neil Danielson, Jason Berberich,  
Catherine Almqvist  
Miami University**

Perfluorooctanoic acid (PFOA) is a persistent and recalcitrant organic contaminant of exceptional environmental concern, and its removal from wastewater has increasingly attracted global attention due to the grim ambient distribution and strong bioaccumulation of PFOA. A controlled particle and pore size polystyrene-divinylbenzene weak anion exchange polymer (PSDVB-WAX) having primary and secondary amine groups was grafted with a co-polymer of chlorotrifluoroethylene and vinylidene fluoride (Kel-F 800) using potassium t-butoxide in a THF solvent. The intent of combining the Kel-F polymer to the weak anion exchange resin was to accentuate fluorophilic adsorption however the weak anion exchange capability was apparently diminished. We then proposed to employ the same reaction mechanism, grafting polyethyleneimine (PEI) as another amine layer right onto the surface of the fluorinated hydrocarbon weak anion exchange resin. This novel fluorinated hydrocarbon amine weak anion exchange resin displayed effective sorption of PFOA based on breakthrough studies with 2 cm polymer packed columns. The breakthrough for the PSDVB-WAX-Kel-F-PEI polymer was about factor of 1.8 better than the PSDVB-WAX starting material and a factor of 2.3 better than the PSDVB-WAX-KEL-F product. The PFOA sorptive capacity of the novel sorbent is directly proportional to PEI amounts added within the synthesis. The adsorption kinetic parameters, determined using the Thomas model and the Yoon-Nelson model, were obtainable from the breakthrough curves for the optimum grafted polymers and will be compared to those found using the PSDVB-WAX starting material column and an activated carbon packed column.

3:55 pm

**“Developing a Robust Extraction Method for the Determination of Per- and Polyfluoroalkyl Compounds (PFASs) in Tissue Followed by Ultra High Performance Liquid Chromatography-Tandem Mass Spectrometry Analysis”**

**Grace Greene, Crystal Vu, Christian Pyle, Isabelle Razon, James Stuart, Anthony Provatas, Christopher Perkins  
University of Connecticut**

Per and poly- fluoroalkyl compounds, or PFASs, are a class of environmentally persistent compounds especially resistant to degradation. PFASs have the ability to spread out in a thin film across flammable liquids, so they are often used in specialized firefighting foams called AFFFs (aqueous film forming foams.) These firefighting foams are used on air bases, airports, and firefighting training facilities. They become introduced into the environment when extinguishing crash fires and during training exercises. Because of the adverse health effects associated with high concentrations of PFASs in tissue, including certain cancers, reproductive issues, and liver and kidney toxicity, analysis of extracted PFAS concentrations is critical to mitigating human exposure to these chemicals.

This project analyzed liver and muscle tissue from deer living in the forest surrounding a former New England military air base that used AFFFs. There is at this time, no standardized procedure for PFAS extraction from tissue, so the procedure used was derived from EPA method 537.1 for extracting PFAS from drinking water. Following extraction, the supernatant was analyzed using Ultra High Performance Liquid Chromatography Tandem Mass Spectrometry (UHPLC-MS/MS) for fourteen PFAS compounds. The reporting limits ranged from 0.45 to 26.8 ng/g. Four of the thirty one deer tissue samples had a detectable PFAS concentration.