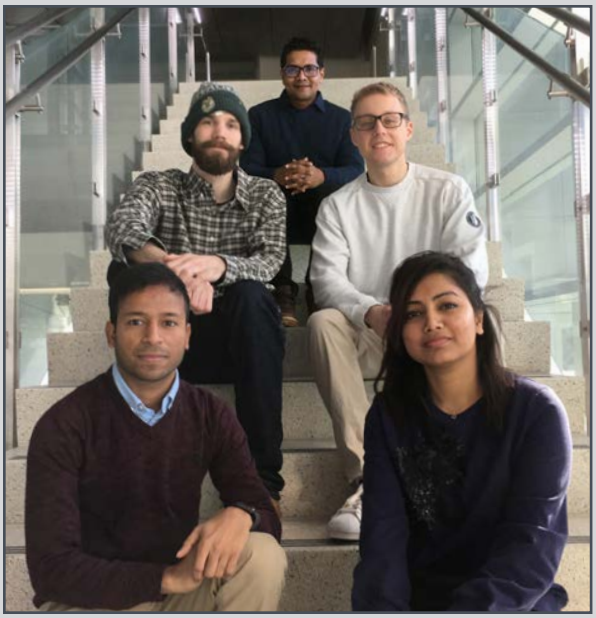
# CHEM/BIOCHEM

Newsletter for Alumni and Friends

Spring 2019



This semester, we welcomed five new graduate students. During their first semester, the new students will rotate through different labs before choosing which research group they will join. They are also diving head first into coursework and teaching laboratory sections. Welcome and keep up the good work!

*Stephen Baldwin, Laboratory Technician*

We are also excited to welcome our new Laboratory Technician, Stephen Baldwin. Steve supports our organic chemistry and general chemistry curriculum. Welcome, Stephen!

*New students, clockwise from top: A.F.M. Towheedur Rahman (Doctoral, Organic/Medicinal), Ian Schwartz (Master's, Analytical), Dishary Sharmin (Doctoral, Organic/Medicinal), Taufeeque Ali (Doctoral, Organic), and Christopher Harris (Doctoral, Analytical).*

## From the Chair's Desk

Joe Aldstadt

We hope you are well. We've been busy as usual — our programs continue to thrive. Highlighted in this issue are research projects in Professor Shama Mirza's lab describing her novel bio-analytical approaches to the study of brain tumors and in Professor Jian Chen's group in developing innovative materials for stimuli-responsive structural coloration.

After 45 years of dedicated service to the department, Distinguished Professor Jim Cook retired at the end of December. Jim was without question a major force in building the department to the current R1-level of scholarship. Jim will certainly be missed but will lend his expertise to furthering programs that he pioneered in our Milwaukee Institute of Drug Discovery.

Progress in realizing our new building continues at a rapid pace, as presently the Governor's proposed budget lists it as the #1 priority in new construction in the UW System (budgeted at $130M). An architectural & engineering firm was contracted recently so the design phase is now underway; the initial estimate for occupancy is 2022-3. We recently hosted a news conference in which Chancellor Mark Mone, UW System President Ray Cross, Tim Sheehy of the Metropolitan Milwaukee Association of Commerce, and Julia Taylor of the Greater Milwaukee Committee spoke of the significant impact that the new facility will not only have upon our work on campus but also for the long-term economic effect, particularly on the growth of STEM-related businesses in the Milwaukee area and beyond.

Finally, our annual Research Symposium & Awards Day will be held on Friday, April 26th. Our speaker for the Sosnovsky Symposium will be Prof. Margaret Brimble from the University of Auckland, New Zealand and her talk is entitled: "Nature's Medicine Chest: Opportunities for Synthesis and Drug Discovery". So mark your calendar and we hope that you will be able to attend!

Sincerely,

Joe

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College of Letters & Science

## Department Hosts First Analytical Chemistry Conference

In January, the Department and the Milwaukee Institute of Drug Discovery held the inaugural Milwaukee Analytical Chemistry Conference (MACC): Mass Spec at Your Finger Tips. Despite the frigid weather with wind chills well below zero, nearly 100 scientists traveled from local and regional institutions to attend. The all-day conference kicked off with "Mass Spectrometry-Based Investigations of Antibody Glycosylation" by Prof. Catherine Costello, William Fairfield Warren Distinguished Professor of Biochemistry at the Boston University School of Medicine. Professor Costello discussed the power of mass spectrometry for the analysis of glycans and glycoconjugates in high-throughput methods. She discussed how, in addition to traditional collision-induced dissociation, the use of activated electron dissociation provides more efficient cross-ring cleavages for glycoconjugates. Finally, she described what she foresees as the future of glycan and glycoconjugate analysis; the combination of ion mobility spectrometry with tandem mass spectrometry to provide unprecedented selectivity and sensitivity in "glyco-mapping" research.

Afterwards, as attendees set up for the poster session, representatives from Accelerated Analytical Laboratories, Aerotek, ThermoFisher, and Eurofins Scientific were on hand to answer questions. The next keynote speaker was Prof. Brandon Ruotolo, Professor of Chemistry from the University of Michigan. Professor Ruotolo presented "Structural Biology in the Gas Phase: Rapid Analysis of Protein Complex Sequence, Stability, and Structure." He discussed mass spectrometry techniques that his group has pioneered that are designed to improve the accuracy of biomolecule structure elucidation, an area that is relatively underdeveloped in current bio-pharmaceutical research. He presented recent developments in ion mobility-mass spectrometry that measure the stability and unfolding pathways of gas-phase proteins. One interesting note: during the question and answer period, Brandon noted that much of the research he had presented had been conducted by Joe Eschweiler, who received his Ph.D. from Michigan last year and is now a staff scientist at AbbVie (formerly Abbott Laboratories). Joe received his B.S. in Chemistry from UWM in 2012. Yes, it is a small world!


### Save the Date

Research Symposium and Sosnovsky Lecture

Join us on Friday, **April 26, 2019** in the **Kenwood IRC Atrium** to celebrate our students' hard work and view the incredible showcase of undergraduate and graduate research from this academic year.

After the poster sessions, Prof. Margaret Brimble from the University of Auckland will give a talk as part of the annual Sosnovsky Lecture Series in **CHM 190**. For more information, visit bit.ly/symp-sos.

The conference also hosted three workshops. The workshops included morning and afternoon sessions so that attendees could attend two of them. Amy Furreness from Shimadzu presented a workshop on "High Throughput Analysis of Drug Toxicology", John Butler from Thermo-Fisher Scientific presented "New Solutions for LC/MS Optimization" and Margaret Guthrie, a UWM alumna from Phenomenex presented "Solid Phase Extraction Techniques for Sample Preparation". Guanguan Li, who attended the Shimadzu workshop said she "got a chance to see how people were actually using the software to do data analysis and extraction from a big database step-by-step, as well as how to set up specific methods for toxicity studies, which was brand new to me."

The conference concluded with an undergraduate and gradu-

ate student poster session. Heather Leskinen from the Department of Biological Sciences at UW-Milwaukee won first place for the graduate student poster entitled “Searching for cJun Dimerization Partners that Promote Regeneration-Associated Gene Expression after CNS Injury." The second graduate student poster award went to Melissa Pergande, a chemistry student from the Laboratory of Integrative Neuroscience at the University of Illinois-Chicago. Her poster entitled “Quantitative, Label-Free Proteomics in the Symptomatic Niemann-Pick, Type C1 Mouse Model Using Standard Flow Liquid Chromatography and Thermal Focusing Electrospray Ionization." As for the undergraduate category, Marwat Salamin and Petra Stevanovic, who work with Dr. Mirza in the Chemistry & Biochemistry Department, won first place with their poster entitled "Identification of urinary biomarkers for the early diagnosis of UPJO using ICP-MS."

Overall, the conference was a remarkable success as attendance not only exceeded our initial estimates but also included representation from a wide variety of fields, ranging from pharmacology to environmental sciences. We have received positive feedback, such as from Professor Dave Petering, who attended the Thermo Fisher workshop, who reflected: "I attended the morning lecture on the application of mass spectrometry to the determination of oligosaccharide modifications of proteins and one of the workshops that followed on the methodology behind other state-of-the-art biological applications. UWM is now a hotbed of mass spectrometry with its installation of major instruments that is unsurpassed in the region. Thus, it was no surprise that we attracted two outstanding experts in this research area to speak as well as excellent personnel from instrument companies to lead workshops." We are already planning for next year’s conference and are brainstorming ideas for a new theme. If you attended this year’s Milwaukee Analytical Chemistry Conference and would like to provide feedback, please do so here: bit.ly/MACC-survey.

## Fall 2018 Doctoral & Master's Degrees

### Doctoral

Heli Fan (Peng Group): “Inducible DNA Cross-Linking Agents: Design, Synthesis, Mechanism, and Anticancer Activity”

- Heli is a Research Associate for Prof. Peng and will be returning to China as an Assistant Professor at Tianjin Medical University this fall.

Matthew Hoag (Moran Group): “Renalase as an Intracellular Metabolite Repair Enzyme”

- Matthew is currently a Post-doc in Michael Toney's lab at the University of California, Davis.

Md. Toufiqur Rahman (Cook Group): Part I “Shorter and Improved Access to the Key Tetracyclic Core of C-19 Methyl Substituted Bioactive Sarpagine-Macroline-Ajmaline Indole Alkaloids"
Part II “The Total Synthesis of a Number of Bioactive C-19 Methyl Substituted Macroline-Sarpagine Indole Alkaloids”

- Toufiqur joined The Research Triangle Institute (RTI International, Durham, NC) as a Post-Doctoral Fellow in January.

### Master’s

Victoria Fisher-Keough (Murphy Group): “From General Chemistry to Anatomy and Physiology: Revalidating and Adapting Assessments and Models”

- Victoria is currently the Jewel's Scholar Tutor at Mount Mary University and a Faculty Assistant at UWM.

Kelly Pauly (Arnold Group): “Proposal to Validate Groups Of Materials, Rather Than Individual Material, For USP <233> elemental Impurities Analysis By ICP -MS”

- Kelly is a manager at Eurofins SF Analytical, supervising a group of QC chemists running specialty testing on raw materials.

# Mirza Group Makes Progress in Unlocking Answers to Glioblastoma

Hope for treating the kind of brain cancer that took the life of U.S. Senator John McCain lies with a compound, identified by researchers at UWM and the Medical College of Wisconsin (MCW), that slows the growth of this aggressive cancer, called glioblastoma. But in finding the compound, UWM Professor Shama Mirza admits, luck was on the researchers' side. They weren't expecting to uncover a potential new treatment option for a cancer with a median survival period of 15 months. They began, instead, with a more modest objective: they wanted to predict which patients would benefit from chemotherapy and radiation treatment and which would not.


Shama Mirza

Mirza, who joined our faculty in 2016, first encountered glioblastoma while working at MCW. She was on a team that supported oncologists as they treated patients. Team members noticed that some patients developed resistance to treatment, and, once that happened, their tumors reappeared more aggressively than before and they died much sooner.

"Knowing who would benefit from the treatments and who would not – that is the guessing game we are playing now," says Mirza, an Assistant Professor who also directs the Shimadzu Laboratory for Advanced and Applied Analytical Chemistry at UWM. The information would help physicians better advise patients on treatment decisions.

Using mass spectrometry, the researchers, including Kathleen Schmainda and Christopher Chitambar at MCW, scanned 600 proteins, looking for ones involved in the progression of glioblastoma, particularly one that would act as a biomarker for the more treatment-resistant version of the disease.

## Department in the News

- In-Focus Magazine did a feature on Prof. Anja Blecking's work as a co-PI for the Milwaukee Master Teacher Partnership (MMPT). Check it out here: bit.ly/Blecking-MMPT.
- Prof. David Petering was quoted in two articles regarding the environmental impact of Foxconn. Read them here: bit.ly/Petering-MJS and bit.ly/Petering-UM.
- Department faculty and graduate students advocated for a new Chemistry Building, read about it here: bit.ly/New-Bldg.

Identifying a protein biomarker is an important step in drug development. "Proteins are the ultimate drug targets because they are responsible for so many life processes" Mirza said. Their search turned up a protein with far greater promise than being an indicator of drug resistance because it is involved in the cancer's growth. Armed with a target, the researchers' next step was to search hundreds of existing compounds for those that block the protein, something current treatment does not do effectively. And they found a match. The compound they are now testing to fight glioblastoma has been used in Japan since the 1980s to treat colorectal cancer. Better still, the compound crosses the blood-brain barrier, which had been a major obstacle in improving glioblastoma treatment. Mirza estimates the animal testing will continue for at least several more years before they can apply for human trials.

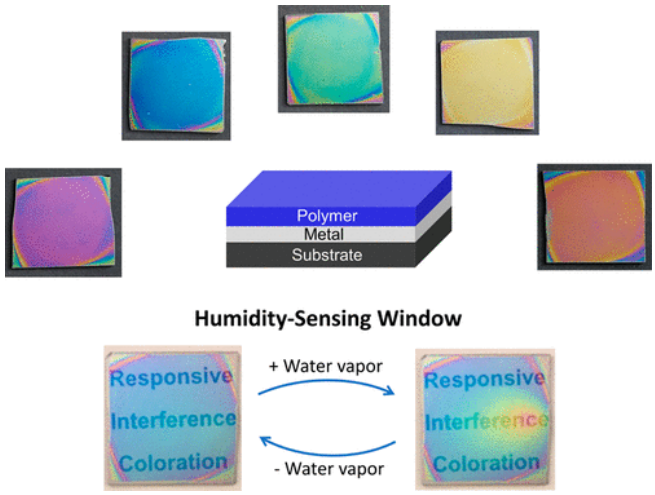
"But," she says, "if the results of human trials agree with our current findings, it's going to be huge for these patients."

Read the original UWM Report article here: bit.ly/Mirza-Glioblastoma. Prof. Mirza and Dr. Douglas Stafford also spoke about their glioblastoma research in an interview with WUWM 89.7. Listen here: bit.ly/Mirza-Stafford.

# A Versatile Strategy for Transparent Stimuli-Responsive Interference Coloration

The bioinspired stimuli-responsive structural coloration has received great interest from the scientific and engineering communities in the past two decades, and it offers a wide range of promising applications in medical diagnostics, advanced packaging, environmental and building monitoring, adaptive camouflage, intelligent coatings and textiles, and anti-counterfeiting.

While remarkable progress has been made in the field of responsive structural coloration based on photonic crystals and multilayer interference, how to make high-quality responsive structural coloration systems on a large scale at low cost still remains a challenge. Thin-film interference is the simplest structural coloration mechanism, which is responsible for the colorful, iridescent reflections that can be seen in oil films on water, and soap bubbles. Owing to its design simplicity, which does not require multilayers of materials with alternative refractive indices or micro- and nanostructures, thin film interference represents a promising solution towards scalable and affordable manufacturing of high-quality responsive structural coloration systems.




However, thin films of polymers with appropriate thickness generally do not exhibit visible structural colors if they are directly deposited on transparent substrates such as glass. Seyedali Banisadr (Ph.D., 2018), Adebola Oyefusi (Ph.D. candidate), and Prof. Jian Chen have developed a versatile new strategy that enables scalable and affordable manufacturing of transparent Stimuli-Responsive Interference Coloration (RIC) systems. They have demonstrated real-time, continuous, colorimetric RIC sensors for humidity, organic vapor, and temperature by using various stimuli-responsive polymers. The main advantages of such RIC sensors include low cost, zero power consumption, spatial and temporal resolution, and a fast, dynamic, and reversible response. The selectivity of a RIC sensor towards a specific stimulus can be modulated by choosing a polymer material with desirable structure and properties. Using a clear substrate (e.g., glass) allows for strong coupling of reflected colors and complementary transmitted colors on opposite sides of the transparent RIC film, which leads to new potential applications such as a self-reporting, humidity-sensing window without consuming power. Potential application examples include outdoor monitoring of the indoor relative humidity that enables facile control of the indoor humidity by a third party without compromising of security, indoor monitoring of the outdoor air humidity that helps residents to easily determine when to open windows for fresh air with suitable relative humidity, real-time monitoring of potential window leaks with spatial resolution that is crucial for sealing the leaks and saving energy, and monitoring of the air humidity inside or outside the automobile to help drivers prevent the car window from fogging up by timely adjustment of humidity and temperature inside the car. Although the current work is focused on rigid, transparent glass, their RIC design is applicable to many other substrates such as polydimethylsiloxane. Since a vast number of stimuli-responsive polymers and composites are available, it is possible to significantly expand the RIC systems with new properties and functions, which will open the door to many application possibilities. To read the full article that was published in ACS Applied Materials & Interfaces, visit bit.ly/Chen-RIC.


Seyedali Banisadr

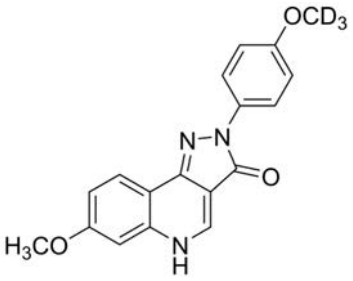

Adebola Oyefusi

## Graduate Student Spotlight: Daniel Knutson


Daniel Knutson

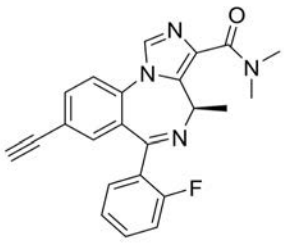
Inspired by the loss of his first wife to a prescription drug overdose, Chemistry & Biochemistry graduate student, Daniel Knutson joined the Cook Group in 2015 to "do something about it." Sadly, Dan's personal loss is an increasingly common story as the opioid and benzodiazepine epidemic is on the rise, claiming 1,100 deaths in 1999 and increasing to over 11,000 deaths in 2017, according to the CDC. Given the Cook Group's long-standing history of successfully searching for new ligands (potential new drugs) that selectively interact with specific subtypes of GABAA receptors (GABAARs), joining the group was a natural fit for Dan. The problem with current neurological drugs on the market is that they lack functional selectivity, meaning that in addition to the desired receptor or receptor subtype of interest, these drugs also target undesired receptors causing serious side effects. For example, the commonly prescribed benzodiazepine, alprazolam, is used to treat anxiety and panic disorders but also causes side effects such as sedation, ataxia, and amnesia, as well as euphoria, which can lead to addiction. Alprazolam interacts with four of the major GABAAR subtypes (a1, a2, a3 and a5) and therefore is not considered functionally selective. Dan's research piggy-backs on the work of many years of students in the Cook Group and focuses on discovering ligands functionally selective for a5- or a6-containing GABAARs.

Dan's work on the design and synthesis of the first and only a6-selective ligands in the world was featured in the Journal of Medicinal Chemistry (J. Med. Chem. 2018, 61, 6, 2422-2446). Deuteration of certain pyrazoloquinolinones originally synthesized in 1995 by the Cook group revived these ligands as drug candidates by increasing their metabolic stability by utilization of the kinetic isotope effect (KIE) and thereby doubling the concentration that reaches the brain. The continuing studies on the lead compounds from this work with collaborators in Austria, Serbia, and Taiwan illustrate the promise these deuterated pyrazoloquinolinones exhibit in treating migraines (Neuropharm. 2018, 140, 1-13), trigeminal pain (Eur. J. Pain. 2019, published on-line), and schizophrenia (Br. J. Pharmacol. 2018, 175, 2414-2427). More recently, the key lead compound DK-I-56-1 has been shown to be active against disorders such as Tourette's syndrome.



DK-I-56-1

In a different area, imidazodiazepines (such as GL-II-73) designed as a5-subtype selective ligands at GABAARs have shown promise in the area of memory loss and depression (Mol. Neuropsychiatry. 2019, published online). Here, Dan's work has involved the process development of the chemistry to more reliably synthesize these a5-selective imidazodiazepines on 50 to 100-gram scale for toxicology and efficacy studies. These potential drugs were first discovered by fellow Cook group member, Guanguan Li. This work is supported by a collaboration with the Center for Addiction and Mental Health (CAMH) at the University of Toronto.



GL-II-73

The key to the success of both these projects has been the Milwaukee Institute of Drug Discovery (MIDD) and the Shimadzu Laboratory for Advanced and Applied Analytical Chemistry, where compound characterization and metabolic stability assays relied heavily on the new state-of-the-art LCMS-IT-TOF and Triple Quad LCMS-8040 mass spectrometers. Additionally, the new 500 MHz Bruker NMR spectrometer was also an important and powerful tool for compound characterization. At the MIDD, the in-house capabilities ena-

ble Dan and the Cook Group to assess hepato and renal toxicities by in vitro cytotoxicity assays and in vivo sedation and motor activity on the rotarod.

By design, these a5-targeting imidazodiazepines and a6-targeting pyrazoloquinolinones are functionally selective, positive allosteric modulators (PAMS) for the GABAAR subtype of interest. Thus, these novel ligands are devoid of the sedative, amnesic, euphoric, and ataxic side effects associated with current GABAergic drugs on the market today. The next step is to collaborate with investors to carry the compounds into Phase 1 clinical trials where Dan hopes to further show that he indeed "did something about" the opioid and benzodiazepine epidemic. To read more about Dan and his research, check out the recently published UWM Report article about him at bit.ly/Dan-Knutson.

## Newsletter Going Digital

We are excited to announce that our next issue will be delivered to you digitally so that we can further enhance your experience with a more interactive "look and feel" as well as realize cost savings in the production of the paper version. Half of our current newsletter recipients are already receiving a digital copy. If you would like to continue to receive the *Chemistry & Biochemistry Newsletter* as a hard copy, please write us a short e-mail at chem-info@uwm.edu with your full name, preferred e-mail address and indicate "Newsletter Hardcopy" in message subject. If you do not have e-mail, please contact us at 414-229-3880 and we will ensure that you still receive a paper copy.

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Your contributions enhance the educational experience of our students and strengthen the research and development of our faculty and staff. Please join us in thanking our friends. (Gifts were received from October 2018 to February 2019.)

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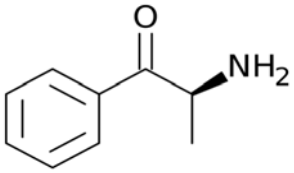
## Undergraduate Spotlight: Lexie Lanphere


Lexie Lanphere

Our Undergraduate Spotlight is on Lexie Lanphere, who is completing her B.S. in Chemistry (with Biochemistry emphasis) and conducting research in the Aldstadt Lab. Lexie, who grew up in Shorewood, came to UWM in 2017 from the University of Kansas, where she had received a B.A. in English. In addition to her chemistry degree, Lexie will also be earning certificates (essentially "minors") in Forensic Science and Forensic Toxicology. At Kansas, Lexie was a member of the Division I Crew team, where she had a four-year scholarship. Lexie is continuing her passion for rowing by serving as the head coach of the women's team of the Milwaukee Rowing Club.

Lexie began her research last summer and has received several grants from UWM's Office of Undergraduate Research (OUR) through their Support for Undergraduate Research Fellows (SURF) program, which has been a key source of support for many years throughout the department. Her research focuses on developing new analytical methods for measuring "designer drugs" by flow-based proton NMR methods. It is crucial for crime labs to have fast, automated methods to allow for the unequivocal identification of drugs of abuse. This project, through support by UWM's Research Growth Initiative, is a collaboration between John Frost (Ph.D., Analytical-Physical, 2011) at ThermoFisher and Sandy Koresch at the Wisconsin State Crime Lab (WSCL) in Milwaukee. Methods are being studied which interface Sequential Injection Analysis (SIA) to ThermoFisher's picoSpin80 NMR spectrometer. Lexie's work involves study of cathinones (more commonly known as "bath salts") which are beta-keto substituted derivatives of amphetamine.

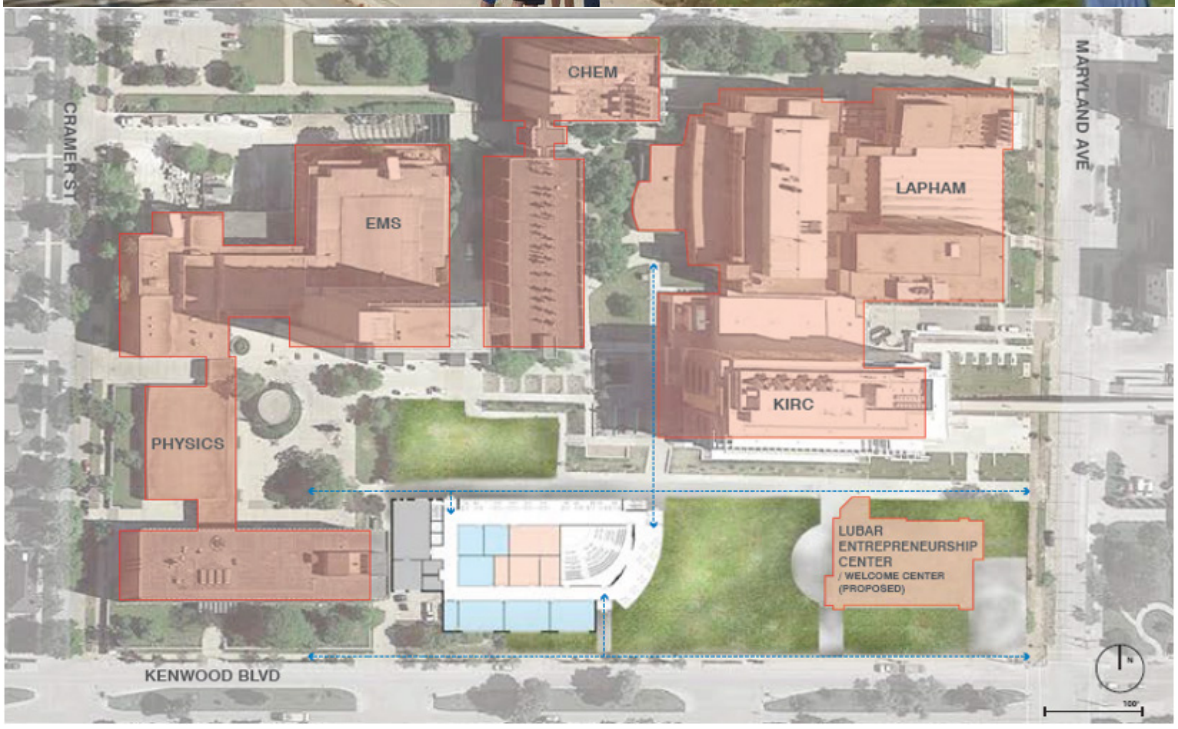



The SIA methods under development include solid-phase extraction (SPE) using selective cation-exchange resins and liquid-liquid extraction (LLE) in a novel on-line design in which the slower moving, more viscous organic phase (hexanol) creates a "pseudo-stationary phase" through which the faster moving, less viscous aqueous (sample) phase passes through. The NMR method provides, of course, very high selectivity for the isolated zones from the SIA that contain cathinones. Additionally, a degree of pre-concentration is realized in both the SPE and LLE methods such that detection limits on the order of ~1 mM are realized, a level which more than suffices for the levels typically found in confiscated samples. Testing of the SIA-NMR method at UWM involves simulants of the cathinones, but testing at WSCL conducted last summer along with Tim Trinklein (B.S., Chemistry, 2018), now a first-year graduate student in the Department of Chemistry at the University of Washington in Seattle, was successful in measuring several cathinones in authentic samples. In addition to the SIA-NMR work at WSCL last summer, Tim and Lexie also developed a method based upon reversed-phase LC interfaced to (off-line) proton NMR, in which select peaks in the chromatogram are diverted following UV detection to the NMR flow cell for quantitation. Future work will focus on further study of the LC-NMR method and application of the SIA-NMR methods to other illegal drugs such as fentanyls.

In addition to learning analytical method development and developing expertise in flow-based techniques and in the interpretation of NMR spectra, Lexie has also learned the fundamentals of experimental design and multi-variate method optimization as part of her studies. Additionally, her work was presented last October at the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) meeting in Atlanta, and she will present her research in May at the ACS Great Lakes Regional Meeting in Lisle, IL. Lexie's coursework and research are preparing her well for her career goal of becoming a scientist in a forensic laboratory.

# New Chemistry Building

Replacement of the current Chemistry building and the associated central utility system extensions are only a few approvals away. Here is an example of what a new Chemistry building might look like.




Community Design Solutions School of Architecture & Urban Planning University of Wisconsin-Milwaukee. *UWM Chemistry Gateway to STEM*, May 2017.

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