

Topic: “New Technologies in Ambient Mass Spectrometry and Their Applications in Rapid Food Screening, Analyzing pL Sample, Identifying Novel Intermediate, and 3D Surface Imaging.

Ambient ionization mass spectrometry (MS) analyzes ions directly from native samples with minimum preparation. In this talk, we will present one application in food analysis and several recent developments.

Analyzing food matrices involve complicated sample preparation procedures. Direct ionization or direct infusion of food sample are usually associated with serious carry-over contamination and ion suppression. To overcome these, food (caramel color) samples were analyzed by paper-spray ionization in this work. A sample was dropped onto the center of a paper triangle. Then, the solvent was supplied at the base of the paper triangle while electrospray ionization being generated at the tip of the paper triangle. Analytes were extracted by the solvent flow, and ionized by the electrospray. The porous paper substrate is disposed after each sample run, avoiding potential carry-over contaminations.

Unstable ion current from ion source would affect the quality of multiple reaction monitoring (MRM) quantitation, which is augmented in the ambient ionization of complicated food samples.

To address this problem, an ion trap tandem MS was developed to simultaneously isolate and fragment both the analyte and internal standard. Fluctuations in ion currents were cancelled in this ion trap simultaneous MRM (s-MRM) experiment, achieving improved precision for quantitation on an ion trap instrument. Rapid qualitative and quantitative analysis of 4-methylimidazole (4-MEI) in caramel and beverage samples is demonstrated using this method.

The minimum level of 4-MEI detectable was $5 \text{ pg } \mu\text{L}^{-1}$ in the caramel matrix. 11 caramel samples were analyzed with effective quality control measure. Relative standard deviations were less than 15% and the linear dynamic range was three orders of magnitude.

Besides providing lower cost analytical protocols which are also faster, ambient mass spectrometry also pushes the development of MS technology, partially by staying away from the advantages of separation. This talk will also briefly showcase several recent developments such as low volume (pL) sample ionization, zeptomole sensitivity, nanocoulomb charge delivery, labile intermediate identification, and MS imaging of 3D surfaces. Potential new regimes in separation that can be coupled with these new MS technology will be discussed.

Dr. Anyin Li

Georgia Institute of Technology, School of Chemistry & Biochemistry
Atlantic Drive, Atlanta, GA 30332
anyin.li@chemistry.gatech.edu (765)237-1695

EDUCATION

Purdue University (West Lafayette, IN) Ph. D. in Analytical Chemistry, Aug. 2014
Advisor: Professor R. Graham Cooks
Dissertation: Mass spectrometry for ambient analysis, Titan atmosphere chemistry and synthesis of nanoparticles
Beijing Normal University (Beijing, China) B. S. in Chemistry, June 2008

RESEARCH INTERESTS

- Fundamental and application of ionization processes
- Ion chemistry for analysis and nanofabrication
- Novel mass spectrometry methods for qualification and quantitation
- Design of sampling probes for high throughput mass spectrometry analysis
- Coevolution of Robotics and Analytical Chemistry

RESEARCH EXPERIENCE

NSF/NASA Center for Chemical Evolution, Georgia Institute of Technology, Atlanta, GA (Sep. 2015 – present)

Postdoctoral Fellow, Advisor: Professor Facundo Fernández

- Rational nano-Coulomb ionization for highly efficient MS analysis
- Robotic sampling and ionization for the MS analysis of irregular surfaces
- Designing analytical protocols for lipids relevant to chemical evolution of life origin

Purdue University, West Lafayette, IN (Aug. 2008 – Aug. 2015)

Post Doctorate Fellow (2014-2015) & Graduate Student (2010–2014),

Advisor: Professor R. Graham Cooks

- Electrospray of nonpolar solvent and hydrocarbon analysis (funded by NSF)
- Gas phase PAH ion chemistry simulating Titan atmosphere (funded by NASA)
- Double-blind quantitative analysis of food contaminants (funded by Coca-Cola)
- Noble metal ionization for nanoparticle and organometallic synthesis (funded by DOE)

Indian Institute of Technology Madras, India (Jan.-Mar. 2014)

Visiting Scholar, Principle investigator: Professor T. Pradeep

- Nanostructure modification of surfaces using ambient ion beams

University of Liverpool, UK (Nov. 2013, Jul. 2015)

Visiting Scholar, Principle investigator: Professor Stephen Taylor

- Crude oil component analysis using portable MS
- Protocols for explosive analysis using portable MS equipment

TEACHING & MENTORING EXPERIENCE

- Teaching assistant for Chem 115 (2008-2009, Undergraduate Course, 48 students)
- Teaching assistant for Chem 257 (2009-2010, Undergraduate Course, 48 students)
- Student mentoring
Graduate students: Michael Wleklinski, Dr. Pu Wei, Adam Hollerhach
Undergraduate student: Jason Wu

JOURNAL REFEREE

Journal of Chromatography A, Nature Communication, Scientific Report, Food Analytical Methods, Electrochimica Acta, Journal of The American Society for Mass Spectrometry, Langmuir

PUBLICATIONS

1. **Anyin Li***, Yunlong Zi*, Hengyu Guo, Zhong-Lin Wang, Facundo Fernández. Rational Triboelectric nanogenerators for sensitive nano-coulomb molecular mass spectrometry Nano-Coulomb Ionization. *Nat. Nanotechnol. Online*, DOI: doi:10.1038/nnano.2017.17 ;
2. Depanjan Sarkar, Maheswari Mahitha, Anirban Som, **Anyin Li**, Michael Wleklinski, Robert Graham Cooks and Thalappil Pradeep. (2016) Metallic Nanobrushes Made using Ambient Droplet Sprays. *Adv. Mater.* 28, 2223-2228.
3. Fred Jjunju, Simon Maher, **Anyin Li**, Sarfaraz U. Syed, Barry Smith, Ron M. A. Heeren, Stephen Taylor, and R. Graham Cooks. (2015) Hand-Held Portable Desorption Atmospheric Pressure Chemical Ionization Ion Source for in Situ Analysis of Nitroaromatic Explosives. *Anal. Chem.* 87, 10047-55.
4. **Anyin Li**, Adam Hollerbach, Qingjie Luo, R. Graham Cooks. (2015) On-demand Ambient Ionization of Pico-liter Samples using Charge Pulses. *Angew. Chem.* 54, 6893-6895.
5. Fred Jjunju, Simon Maher, Abraham Tawiah, **Anyin Li**, Stephen Taylor and R. Graham Cooks. (2015) Analysis of Polycyclic Aromatic Hydrocarbons using Desorption Atmospheric Pressure Chemical Ionization Coupled to a Portable Mass Spectrometer. *J. Am. Soc. Mass Spectrom.* 26, 271-280.
6. **Anyin Li**, Zane Baird, T. Pradeep, R. Graham Cooks. (2014) Using Ambient Ion Beams to Write Nanostructured Patterns for Surface Enhanced Raman Spectroscopy. *Angew. Chem.* 53, 12528-12531.
7. **Anyin Li***, Qingjie Luo*, So-Jung Park and R. Graham Cooks. (2014) Synthesis and Catalytic Reactions of Nanoparticles formed via Electrospray Ionization of Coinage Metals. *Angew. Chem.* 53, 3147-3150.
8. **Anyin Li**, Fred Jjunju, and R. Graham Cooks. (2013) Nucleophilic Addition of Dinitrogen to Aryl Cations in the Gas Phase. *J. Am. Soc. Mass Spectrom.* 24, 1745-1754.
9. Fred Jjunju, **Anyin Li**, Abraham Badu-Tawiah, Pu Wei, Linfan Li, Zheng Ouyang, Iman S. Roqan and R. Graham Cooks. (2013). *In situ* Analysis of Corrosion Inhibitors Using a Portable Mass Spectrometer with Paper Spray Ionization. *Analyst.* 138, 3740-3748.
10. **Anyin Li**, Pu Wei, Hsu-Chen Hsu, R. Graham Cooks. (2013) Direct Analysis of 4-Methylimidazole in Foods using Paper Spray Mass Spectrometry. *Analyst.* 138, 4624-4630.
11. Fred Jjunju, AK. Badu-Tawiah, **Anyin Li**, Santosh Soparawalla, Iman S. Roqan, R. Graham Cooks, (2012) Hydrocarbon analysis using desorption atmospheric pressure chemical ionization. *Int. J. Mass Spectrom.* 345, 80-88.
12. AK Badu-Tawiah, **Anyin Li**, Fred Jjunju, R. Graham Cooks (2012). Peptide Cross-linking at Ambient Surfaces by Reactions of Nanosprayed Molecular Cations. *Angew. Chem.* 51, 9417-21.
13. **Anyin Li**, He Wang, Zheng Ouyang and R. Graham Cooks. (2011) Paper spray ionization of polar analytes using non-polar solvents. *Chem. Comm.* 47, 2811-2813.

PATENTS

1. Fred P. Jjunju, **Anyin Li**, Abraham K. Badu-Tawiah, Pu Wei, Iman S. Roqan, R. Graham Cooks. "Methods of Analyzing Crude Oil." US Patent (PURD-032/00US 28593/75)
2. **Anyin Li**, Qingjie Luo, and R. Graham Cooks. "Systems and Methods for Producing Droplets including Solvated Metal Ions and Separation of those Ions from an Anion" US Patent (PURD-047/00US 28593/118)

Invited Lectures & Seminar

1. "Mass Spectrometry, let the elephant fly". PUI Seminar Series (CCE outreach program), Chemistry Department, Clayton State University, GA. (April 2017)
2. "Ambient Ionization Methods: Mass Spectrometry Analysis and Nano Fabrication". Chemistry Department Seminar, National Taiwan University, National Dong Hwa University. (Mar. 2016)
3. "The Science and Engineering of Mass Spectrometry: Past, Present and Future". Department of Electrical Engineering & Electronics, University of Liverpool, U.K. (Nov. 2013).

CONTRIBUTED ORAL PRESENTATIONS

1. **Anyin Li**, Anirban Som, T. Pradeep, R. Graham Cooks. "Ionization and Deposition of Gold under Ambient Conditions, a New Precursor for Noble Metal Nanoparticles" *7th International Gold Conference (GOLD2015)*, Cardiff, U.K. (July 2015)
2. **Anyin Li**, Soumabha Bag, Zane Baird and R. Graham Cooks. "Ambient Ion Beams for Nanofabrication" *Turkey Run Analytical Chemistry Conference*, Marshal, IN (Nov. 2014)
3. **Anyin Li**, F. P. M Jjunju, Abraham Badu-Tawiah, Lifan Li, Pu Wei, Z.Ouyang, Iman S. Roqan, and Graham Cooks. "In-situ Analysis of Oil Matrices using Paper Spray Ionization and Portable Mass Spectrometer: Toward Chemical Analysis in the Oil Field of Corrosion Inhibitors and So On". *Chemistry in the Oil Industry XIII: Oilfield Chemistry – New Frontiers*, Manchester, UK. (Nov. 2013)
4. **Anyin Li**, F. P. M Jjunju, Eric Boone, Michael Wlekinski, Kerri A. Pratt, R. Graham Cooks. "Paper Spray Ionization under Harsh Environment and Gas Phase Ion Molecule Reaction under Titan Simulate Environment". *The 9th Harsh Environment Mass Spectrometry Workshop*, St. Pete Beach, FL. (Sept. 2013)
5. **Anyin Li**, Fred Jjunju, R. Graham Cooks. "Polycyclic Aromatic Hydrocarbon Evolution in a Nitrogen Environment Driven by Collisional Activation, Cold Plasma Discharge, or UV Radiation: a Tholin Study." *61th ASMS Conference on Mass Spectrometry conference and Allied Topics*. Minneapolis, MN. (June, 2013).
6. Fred Paul Mark Jjunju, Abraham Badu-Tawiah, **Anyin Li**, Santosh Soparawalla, Iman Roqan, R. Graham Cooks. "Hydrocarbon analysis by desorption atmospheric pressure chemical ionization" *244th American Chemical Society (ACS) National Meeting, Philadelphia, Pennsylvania*. (Sept. 2012).

CONTRIBUTED POSTER PRESENTATIONS

1. **Anyin Li**, Martin Paine, Rachel Stryffeler, Jason Wu, Stephen Zambrzycki, Jake Huckaby, Chu-Yin Chang, Manoj Kumar, Piyoosh Mukhija, Alexander Lambert, Ruffin White, Henrik I. Christensen, Facundo Fernández. "Fully-Automated Ambient Robotic Surface Analysis-Mass Spectrometry" *32nd Asilomar Conference on Mass Spectrometry*. (Oct. 2016).
2. Jason Wu (Undergraduate student), **Anyin Li**, Matt Bernier, Facundo Fernandez. "Ambient Robotic Mass Spectrometry via Cross Platform Synchronization" *64th ASMS Conference on Mass Spectrometry conference and Allied Topics*. (June, 2016).
3. Martin Paine, Rachel Stryffler, **Anyin Li**, Jake Huckaby, Alexander Lambert, Ruffin White, Henrik Christensen, Facundo Fernandez. "Robotic Surface Analysis Mass Spectrometry (RoSA-MS) for Automated Ambient Sampling of Highly-Curved Three-Dimensional Surfaces" *64th ASMS Conference on Mass Spectrometry conference and Allied Topics*. (June, 2016).
4. Joel Keelor, **Anyin Li**, Brian Clowers, Facundo Fernandez. "Coupling of High-Resolution Atmospheric Pressure Drift Tube Ion Mobility Spectrometry with High-Resolution Accurate Mass Orbitrap Mass Spectrometry" *64th ASMS Conference on Mass Spectrometry conference and Allied Topics*. (June, 2016).

5. **Anyin Li**, Adam L. Hollerbach, R. Graham Cooks. "Relay Electrospray Ionization: triggering electrospray using ions and charged droplets for high throughput mass spectrometry analysis" *63rd ASMS Conference on Mass Spectrometry conference and Allied Topics*. (June, 2015).
6. **Anyin Li**, Qingjie Luo, Zane Baird, Depanjan Sarkar, Anirban Som, Bootharaju M. S., Pradeep T., R. Graham Cooks. "Electrospray ionization of noble metals and the collection of metal ions toward the synthesis of metallic nanoparticles and organometallics." *62nd ASMS Conference on Mass Spectrometry conference and Allied Topics*. (June, 2014).
7. **Anyin Li**, Pu Wei, Hsu-Chen Hsu, Linfan Li, Zheng Ouyang, R. Graham Cooks. (2013). Direct Analysis of 4-Methylimidazole in Foods using Paper Spray Mass Spectrometry. *61th ASMS Conference on Mass Spectrometry conference and Allied Topics*. (June, 2013).
8. Fred Paul Mark Jjunju, **Anyin Li**, Abraham Badu-Tawiah, Pu Wei, Iman Roqan, R. Graham Cooks. In-situ Analysis of Corrosion Inhibitors using Paper Spray Ionization Mass Spectrometry. *61th ASMS Conference on Mass Spectrometry conference and Allied Topics*. (June 2013)
9. Pu Wei, **Anyin Li**, Hsu-Chen Hsu, Linfan Li, Zheng Ouyang and R. Graham Cooks. "Direct Analysis of Contaminants in Foods using Paper Spray Mass Spectrometry." *15th Beijing Conference and Exhibition on Instrumental Analysis*. (23rd Oct. 2013)
10. F. P. M Jjunju, **Anyin Li**, Hsu-Chen Hsu and Graham Cooks, Ambient analysis of non-basic Nitrogen Compounds in the Petroleum Oil Using Desorption Atmospheric Pressure Chemical Ionization. *Chemistry in the Oil Industry XIII: Oilfield Chemistry – New Frontiers, Manchester, UK*. (4~6th Nov. 2013)
11. Guannan Li, Vanessa Gallardo, John Nash, **Anyin Li**, Hilikka Kenttämää. A Bracketing Method for Proton Affinity Measurements for Pyridine Radicals and Biradicals. *61th ASMS Conference on Mass Spectrometry conference and Allied Topics*. (June, 2013).
12. Fred Paul Mark Jjunju, Abraham K.Badu-Tawiah, **Anyin Li**, Santosh Soparawalla, Iman Roqan, R. Graham Cooks. Hydrocarbon analysis using DAPCI ionization method. *60th ASMS Conference on Mass Spectrometry conference and Allied Topics*. (2012).
13. Fred Paul Mark Jjunju, Abraham K.Badu-Tawiah, **Anyin Li**, Santosh Soparawalla, Iman Roqan, R. Graham Cooks. *3rd Asian and Oceanic Mass Spectrometry Conference (AOMSC-3), Kyoto, Japan*. (2012).
14. Fred Paul Mark Jjunju, Abraham K.Badu-Tawiah, **Anyin Li**, Santosh Soparawalla, Iman Roqan, R.Graham Cooks. *IET/IOP annual meeting Liverpool University*. (2012)
15. **Anyin Li**, He Wang, Michael Wlekinski (Undergrad), Ryan Espy, Ouyang Zheng, R. Graham Cooks. Paper Spray Ionization using Solvents of Low Polarity or High Viscosity. *59th ASMS Conference on Mass Spectrometry conference and Allied Topics*. (2011).
16. **Anyin Li**, Jinshan Gao, Mingkun Fu, Bartłomiej Jankiewicz, John Nash, Hilikka Kenttämää. Measurement of the Proton Affinities of Dehydro- and Didehydropyridines by Using Gas-Phase Ion-Molecule Reactions. *58th ASMS Conference on Mass Spectrometry conference and Allied Topics*. (2010).
17. Jinshan Gao, **Anyin Li**, John Nash, Hilikka Kenttämää. Substituent Effects on the Reactivity of 3-x-2,4,6-Tridehydropyridinium and 3-X-2,4-Didehydropyridinium Ions (X = Substituent). *58th ASMS Conference on Mass Spectrometry conference and Allied Topics*. (2010).

HONORS, SCHOLARSHIP & AWARDS

• Asilomar Travel Stipend	American Society for Mass Spectrometry	(2016)
• Travel Grant	Savcor Inc.	(2013)
• International Travel Award	College of Science, Purdue	(2013)
• Student Travel Award	Chemistry in the Oil Industry, UK	(2013)
• Ross Fellowship	Purdue University, IN	(2008-2009)
• National Scholarship	Beijing Normal University	(2007-2008)
• Liyun Fellow	Beijing Normal University	(2005-2008)
• 2nd prize National Physics Olympiad	Sichuan Province, China	(2003)