Analytical Chemistry Division

2020
Analytical Chemistry

• Not JUST titrations!

“Analytical chemistry is the art and science of determining what matter is and how much of it exists. In 2012 (salary survey data), analytical chemistry was the most popular field of work for ACS chemists.”

“Analytical chemists use their knowledge of chemistry, instrumentation, computers, and statistics to solve problems in almost all areas of chemistry and for all kinds of industries.”

From the American Chemical Society (ACS)
Analytical Chemistry

• Not JUST titrations!
• We’re doing research in topics as diverse as better batteries, labs-on-chips, forensics, explosives detection and degradation, biofuels analysis, and creating new materials.
• We use almost every instrument you’ve seen plus some.
• Two of the departments’ scanning probe instruments are in the Analytical Division.
Analytical Chemistry Members

- Professor Graham Cheek
- Professor Christine Copper
- CDR Dave Durkin
- Professor Dianne Luning Prak
- Professor Maria Schroeder
- Associate Professor Ron Siefert
- Professor Paul Trulove
RESEARCH INTERESTS
Prof. Graham Cheek
Mi 144  36625 cheek@usna.edu

Electrochemistry of organic compounds

Bio-electrochemistry of amino acids
Cyclic and Square-Wave Voltammetry

Spectroscopic Techniques (NMR, MALDI, UV-VIS)

Solvents : Water, non-aqueous solvents, ionic liquids

Forensic Applications

1. Soil Characterization : X-Ray Fluorescence
2. Paper / Ink Characterization : Voltammetry, Raman Spectroscopy
RESEARCH INTERESTS  Prof. Graham Cheek

Bio-electrochemistry of amino acids

Solvents
pH 5, 7 aqueous buffers
Nonaqueous solvents

Effect of metal ions (Zn$^{2+}$) on electrochemical behavior, especially for “zinc fingers”!

Use of NMR, MALDI, UV-VIS
RESEARCH INTERESTS

Bio-electrochemistry of amino acids

Interaction of Zn$^{2+}$ and other ions such as Bi$^{3+}$ with cysteine and histidine side groups in proteins

Wikipedia, “Zinc Fingers,” accessed 11 February 2018

CHEEK, Graham T., Professor, and WOROSZ, Matthew A., MIDN, “Electrochemical Studies of L-Cysteine,”
RESEARCH INTERESTS

Prof. Graham Cheek

Electrochemical Investigations of Colorants

Flair Blue

BiC Cristal Blue

E, V vs Ag/AgCl

i, μA
Development of Separation and Detection Methods for Forensic Analysis

Prof Christine Copper
ccopper@usna.edu
Michelson 265
Capillary Electrophoresis (CE)

- CE was first used in the early 1980’s.
- Reasonably high sensitivity (ppm or ppb)
- Short separation time (<5 min)
- Small Sample Volume (nanoliters)
- Can be done on a microchip device instead of in a column

*Separation is achieved based on different rates of migration of charged species in an applied electric field.*
Capillary Electrophoresis can be used to detect...

- Explosives in seawater, sand, and soil
- Poisons in beverages
- Ozone in submarine atmospheres
- Nerve agents in atmospheres
- Polyaromatic hydrocarbons in environmental samples
- Carbon monoxide poisoning in blood
- Illicit drugs in urine

- Current students (Goodwin, Dervishian and King) are working on analyzing dyes and their degradation products in fabrics.
Fuel certification program/Office of Naval Research

January 2016
Navy launched Carrier Strike Group out of San Diego powered by mixtures of petroleum-based and bio-based fuel.

http://greenfleet.dodlive.mil/energy/great-green-fleet
Results GC x GC FID
Chemical Composition of JP-5

Navy Jet fuel is a complex mixture of thousands of compounds

Chemical composition, physical properties & combustion of bio-based & petroleum-based fuels

How does chemical structure impact the physical and chemical properties of fuels?

- density
- viscosity
- enthalpy of combustion
- speed of sound
- bulk modulus
- flash point (low flash point compounds)
- surface tension
- heat capacity
- distillation behavior
- enthalpy of vaporization
- combustion in diesel engines

Use of jet fuels in diesel engines → emergency generators/ one-fuel-forward policy

When will the jet fuels fail to combust? (Look at limitations of Mil Spec)

Flash point: How do structural isomers affect flash point?

Recent submission with student
Professor Schroeder’s Research Interests

Office: Michelson 244
Email: schroede@usna.edu

- Analytical Chemistry, Polymer Chemistry
- Laboratory Development
  - Experiments in support of IL or Chemistry of Cooking course
- Chemistry Education Research (CER)
  - Analyzing Plebe Chemistry Curriculum Changes
  - Studies of the Use of Clickers in Plebe Chemistry for Self-Assessment

Laboratory Development

- Previous Experiments developed by Students (used in IL)
  - *Analysis of Foods by Atomic Absorption Spectroscopy* (Tony Ferro, ’05)
    Determination of Iron in Total Cereal by Flame AA
  - *Synthesis and Characterization of Polymer Networks* (Colin Browning, ‘03)
    PDMS Networks, Gluep Swelling, Tensile Strength Viscosity, Crosslinking

- Recent Project
  - *Determination of Heavy Metals in Hyperaccumulator Plants by XRF*

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*Rascio, Plant Science* 2011, 180, 169-181

http://lab-training.com/2013/05/08/introduction-to-aas-component-parts/

https://www.youtube.com/watch?v=Kwau5l7AeM

http://www.horiba.com

Nicole Sarao, ‘19
Chemistry Education Research

- A few years ago, a pilot study on the use of an **Atoms-First** curriculum in Plebe Chemistry was conducted. This year, Plebes are using an Atoms-First textbook.

- Research students involved in analyzing data:
  - Olivia Bair, ’18
  - Clare Suess, ’19
  - Bianca Roach, ’19
  - 1/C Trevor Clark
  - 1/C Sebastian Yocca

- Finishing up analysis and publication
- Work in collaboration with Prof. Dillner, Prof. Teichert, Prof. Bunce
Chemistry Education Research

• **Current Interest** in Plebe Chemistry – Looking at the “Middle Student” – **How can we improve their learning?**

• Self-Assessment during Class – **Clickers**
  • Metacognition (“thinking about your thinking” or “awareness of how you learn”)

• Current Study in Plebe Chemistry (SC112), to continue into the fall semester
  • Treatment (clicker) sections vs Control sections

• Working with both Qualitative and Quantitative data, Statistical Analysis, Coding of Student Responses, Possible Interviews, Development of Clicker Questions

• Collaboration with Prof. Dillner, Prof. Bunce
2016-2017 Project – Nanotubes & Their Applications

Lauren Stiff (2016-2017)

OBJECTIVE: Investigate the ability of nanotubes to encapsulate and stabilize biomacromolecules. Possible applications include: drug delivery, and as a method to protect biomacromolecules from thermal and chemical stresses.

Novel Sorbents (periodic mesoporous organisilicas)

Nick Hutchinson (2012-2013)

- For Analysis of Nitroenergetics (i.e., explosives)
- For Analysis of Perchlorates (used as propellants)
- As a substrate for catalysts to destroy contaminants

Past Projects

Analysis of Explosives - Capillary Electrophoresis
Cody Mendelow (2018-2019)

Micellar electrokinetic chromatography (MEKC) – allows for separation of neutral molecules in an electric field by adding surfactant micelles to the separation buffer.
Simultaneous analysis of hydrophilic and hydrophobic analytes
On-line pre-concentration to improve detection limits

Analysis of Agricultural NH₃ Emissions

Iron in Marine Aerosols

Chesapeake Bay
Ammonia & Nitrate Measurements
Deposition of Nutrients to Surface Waters
Chemistry Evaluation of Printed Inks for Harsh Environments
Collaboration with scientists at Navy Research Laboratory & Air Force Research Laboratory

- Additive manufacturing (AM) has found a wide range of applications in DoD.
- Recent AM successes in the USAF, Navy, and Army include repairs, flight and submarine critical parts, locally certified parts, printed armament, AM cast, and the addition of functionality through AM.
- Conductive inks are an important component in the tool set of AM.
- Conductive inks can be formulated by blending either nanoparticles or micron size particles that are highly conductive such as silver, gold, copper, zinc, or carbon.
- Performance in harsh environments will require enhanced surface adhesion of inks to the substrates.

**Ag nanoparticles-functionalization with poly(vinylpyrrolidone) (PVP)**

1. Reaction mixture
2. Instantaneous nucleation
3. Twinning of nuclei
4. Growth

- Ag\(^+\) ions
- Oxidized –COOH of PVP chain
- Ag atoms
- Ag nuclei
- Twinned Ag nuclei
- PVP chain with terminal –OH
- Ag nanoparticles
- Ag nanoplates
The USNA Ionic Liquids Team

Prof. Paul Trulove  
CDR Dave Durkin  
Dr. Ashlee Aiello  
Dr. Tyler Cosby  
MIDN Christian Hoffman  
MIDN Julia McFarland
Towards Advanced Functional Biopolymer Materials

Paul C. Trulove and David P. Durkin – US Naval Academy

Natural Materials with Dramatically Enhanced Physical and Chemical Properties

**Natural Polymers**
- Natural polymers are renewable materials that have many attractive properties. Some natural silks have strength and toughness comparable to the best synthetic polymers.
- The ability to modify and tailor the shape and properties of natural polymers is limited to nonexistent.

**Ionic Liquids Solvents**
- We have shown that ionic liquids are powerful solvents for the dissolution and processing of a wide variety of natural polymers.
- The solvating ability of ionic liquids provides a powerful tool for the modification and processing of natural polymer materials.

**MAIN ACHIEVEMENTS**
- Synthesized Fe-Pd nanomagnets in a biomaterial matrix and measured their magnetic properties.
- Evaluated the iconicity of ionic liquid-biopolymer solutions showing ion pairing & ion mobility are not significantly impacted by the presence of biopolymer.
- Demonstrated > 1000 fold change in the surface area of welded biomaterials through control of the polarity of the regeneration solvents.
- Developed and applied a Raman spectroscopic method for evaluating the extent of biopolymer reorganization due to ionic liquid treatment.
- Utilized AFM to measure the impact of fiber welding on the nanomechanical properties of biomaterials.
- Synthesized novel polymerizable ionic liquids and demonstrated their in-situ polymerization during fiber welding.

**STATUS QUO**

**NEW INSIGHTS**

**QUANTITATIVE IMPACT**
- Producing natural materials with dramatically enhanced mechanical properties
- Enabling tuneable natural material properties with high spatial resolution
- Integrating functional micro- or nano-materials with catalytic, electrical, magnetic & optical properties into natural fiber matrices

**END-OF-PHASE GOAL**
- Develop multi-functional natural materials and coatings with unique electronic, catalytic, optical, and sensing properties for Air Force and DoD relevant applications in areas such as ballistic protection, energy storage, microelectronics, stealth, laser eye protection, optical computing, chem./bio sensing, in-situ medical applications
## Biopolymer Properties

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Elongation at Failure (%)</th>
<th>Modulus (GPa)</th>
<th>Strength (GPa)</th>
<th>Density (g/cm³)</th>
<th>Energy to Break (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dragline Spider Silk (Nephila clavipes)</td>
<td>10-40</td>
<td>1-30</td>
<td>0.3-1.8</td>
<td>1.35</td>
<td>30-125</td>
</tr>
<tr>
<td>Silkworm Cocoon Silk (Bombyx mori)</td>
<td>15-35</td>
<td>5</td>
<td>0.6</td>
<td>1.45</td>
<td>70</td>
</tr>
<tr>
<td>Nylon 66</td>
<td>18</td>
<td>5</td>
<td>0.88</td>
<td>1.14</td>
<td>80</td>
</tr>
<tr>
<td>Cotton</td>
<td>6-7</td>
<td>6-11</td>
<td>0.3-0.7</td>
<td>1.50</td>
<td>5-15</td>
</tr>
<tr>
<td>Kevlar 49</td>
<td>2.5</td>
<td>124</td>
<td>2.8</td>
<td>1.44</td>
<td>15</td>
</tr>
<tr>
<td>Steel</td>
<td>8</td>
<td>200</td>
<td>2</td>
<td>13.0</td>
<td>2</td>
</tr>
</tbody>
</table>

“Natural Fiber Welding”

Controlled Application of ILs Opens Up the Fiber Structure to Enable Physical and Chemical Modification

Applications of Natural Fiber Welding

- Improve Natural Material Properties
- Controlled Fabrication of Novel Composites
  - Integrate Small Molecules
  - Merge Functional Polymers
  - Entrap Functional Solids
Morphological Influence of Solvent Exchange

MIDN Julia McFarland

**Untreated Cotton**

**MeOH, Water**

**Isopropyl alcohol, Butanone, Cyclohexane**

**Water, Isopropyl alcohol, Butanone, Cyclohexane**

BET Surface Area (m²/g)

- Untreated
- MeOH→H₂O
- IPA→B→CH
- H₂O→IPA→B→CH

**1000× increase**

**10× decrease**

20 µm
Application of Polymerizable Ionic Liquids to NFW

EMIAc
\[
\text{CH}_3\text{N}^+\text{NCH}_2\text{CH}_3^\text{Cl}^-
\]

EMPyrAc
\[
\text{CH}_3\text{N}^+\text{NCH}_2\text{CH}_3\text{O}^-
\]

AMIAc
\[
\text{CH}_3\text{N}^+\text{NCH}_2\text{CH}_2\text{O}^-
\]

AMPyrAc
\[
\text{CH}_3\text{N}^+\text{NCH}_2\text{O}^-
\]

CFM and SEM Images of Welded Cotton Yarns

Polymerization of Ionic Liquid used in Welding

EMIAc + EMPyrAc
\[
\text{CH}_3\text{Cl}^- \quad \text{CH}_3\text{Cl}^-
\]

Initiator
\[
\begin{array}{c}
\text{CH}_3\text{N}^+\text{NCH}_2\text{CH}_3\text{O}^-
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3\text{Cl}^- \quad \text{CH}_3\text{Cl}^-
\end{array}
\]

MIDN Christian Hoffman
Incorporation of Functional Materials via Synthesis with Fiber Particles

**Chemical Modification of Biopolymer, Encapsulated Nanoparticles**

Fiber Particle Modified With Functional Material

Ionic Liquid with Suspended Fiber Particles & Solubilized Polymer

Welded Fibers with Incorporated Functional Material

(Preparation & Temperature)
Synthesis of Functional Nanomaterials in Fiber Powders

Mill to Powder & Dry

Method Used to Produce Fiber Impregnated Nanoparticles

- Pd, Cu, In
- Pd-Cu, Pd-In
- Fe, Fe-Pd
- Ag, Au

Catalytic, Magnetic, Optical

Add Metal Nitrates & Reduce*

Superparamagnetic Fe-Pd NPs in Biopolymer Matrix

- Alloyed nanoparticles (Fe-Pd) form throughout the biopolymer matrix (TEM)
- 5 – 10 nm in size and uniformly distributed (SEM/TEM)

Applications and Future Work

EMI Shielding Development

1. Increase metallic loading ✔ 23 wt% (up from 6-17 wt%)
2. Examine substrate effects ✔ Comparative performance in cotton vs linen
3. Develop welded coatings/structures In process
4. Evaluate shielding performance In process*

*establishing collaboration with NAVAIR
Questions?