John Dorsey Awards Symposium I

Sponsor: ACS Division of Analytical Chemistry
Organizer: John F. Wheeler Furman University, Greenville, SC
Presider: John F. Wheeler Furman University, Greenville, SC

Session Overview: Symposium honoring Professor John Dorsey. Invited and contributed posters and oral presentations.

160. Chiral Capillary Electrophoresis of Transition Metal Complexes: Comparison of Resolving Media and Assessment of Optical Purity

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We have demonstrated the capacity to resolve chiral complexes of transition metals (TM) including $[M(diimine)_3]^{n+}$ complexes using chiral capillary electrophoresis (CCE). Although we have reported excellent separations using antimonyl and dibenzoyl tartrate-based resolving agents for TM systems that incorporate large aromatic ligands, *e.g.*, 2,2' bipyridine (*bpy*), 1,10-phenanthroline (*phen*), or 3,4,7,8-tetramethyl-1,10-phenanthroline (*tmp*), in cases where mixed diimines (*i.e.*, heteroleptic complexes) or bis-diimines are present, these agents may be found inadequate to facilitate effective separation of the respective Λ and Δ isomers. Cyclodextrins (CDs) have been successfully used for many years in CCE applications for optically-active organosolutes; we have discovered that γ and β-sulfated CDs in particular are effective when used in the separation of cationic heteroleptic TM complexes incorporating smaller ligand chemistries. We present here a comparison of the relative strengths and weaknesses of tartrate versus sulfated-CD resolving agents for the chiral electrophoretic separation of several newly synthesized Cr(III) complexes with diverse ligand chemistries.

Optical activity of α-diimine TM complexes is often quantified using circular dichroism (CD) and the associated Δε values taken from the primary literature. The use of CD alone cannot provide an absolute measure of enantiomeric purity in the absence of data obtained for an optically pure reference standard, which are often unavailable. Using a chiral selecting agent in the run buffer, racemic as well as optically active TM complexes have been resolved. Integrated peak areas from optically active (but not optically pure) samples have been used in conjunction with experimentally measured Δε values for the pure isomers.

161. Three Tiers of Value Creation for the Analytical Chemist

James W. Ziegler, Eastman Chemical Company, Kingsport, TN

Unlike energy and matter, economic value CAN be created and destroyed. Value is created when the total benefit delivered is greater than the total cost, including capital, over time. Value is destroyed when the total cost is greater than the total return. Value destruction is not sustainable, and therefore any person or organization focused on success must first understand the primary value-adding activities that it relies upon.

Analytical Chemistry is often viewed solely as a cost to the organization, yet it is important to remember that benefits are delivered. The analytical chemist can create value at three distinct tiers of sophistication - defined here as "Technical," "Strategic" and "Empirical." Definitions and examples of each will be reviewed, along with a discussion of how these are applied for success in the business world.

The relationship between the three tiers of value creation and Dr. Dorsey's accomplishments as a leader in development and application of chromatographic theory, as an outstanding teacher, and as a mentor will be reviewed from this alumnus' perspective.

162. Lessons Learned from Open Access HPLC in GlaxoSmithKline Chemical Development Labs

Steven R. Cole, GlaxoSmithKline plc, Research Triangle Park, NC
Pharmaceutical and Chemical Development analytical scientists typically develop compound-specific chromatographic methods and analyze a heavy proportion of samples generated by formulators and chemists, respectively. In 1999, our company introduced a walkup LC for synthetic chemists in Chemical Development that provided a generic, rapid HPLC analysis for reaction monitoring and initial product purity assessment. Since that time the LC fleet has grown to over 50 instruments used by hundreds of synthetic chemists and is deployed in 6 sites around the globe running over 100,000 samples per year for numerous applications. This talk will focus on managing a fleet of open access LCs and highlight the opportunities for better understanding of method and instrument ruggedness and robustness, optimal maintenance, asset management, and applying lean thinking to the practice of chromatography. The introduction of Zorbax 1.8 micron columns to provide quicker turnaround and higher instrument capacity for the chemists will also be discussed.

163. Liposome Mediated Studies of Membrane Interactions by CE and Calorimetery

Jennifer Carrozzino[1], Jason Barker[2], Suzie Yeh[3], Emnet Yitbarek[3] and **Morteza G. Khaledi**[1], (1)North Carolina State University, Raleigh, NC, (2)KBI BioPharma, Raleigh, (3)NCSU, Raleigh
Liposomes are spherical bilayer aggregates formed in aqueous solution by phospholipids; they are characterized by an interfacial region formed by the head groups of the constituent molecules, a fluid organic region formed by the fatty tails of the lipids, another interfacial region of head groups, and an inner aqueous pool. Due to their structural similarities to biological membranes, liposomes are often used to model cells.

In the first part of this presentation, the usefulness of Liposome Electrokinetic Chromatography (LEKC) for rapid and high throughput screening of drug – membrane interactions as well as for modeling of cell membrane permeability and oral absorption of a series of drugs will be demonstrated. In a related project, the colorimetric shifts in vesicles were utilized for studying membrane partitioning of solutes that lack a UV chromophore.

Finally, the use of CE-LIF as a sensitive and efficient method to study encapsulation efficiency and membrane permeability behaviors of large unilamellar vesicles (LUV) will be discussed.

164. Biphenyl Stationary Phases for Open Tubular Capillary Electrochromatography

G. Brent Dawson and Shelby L. Gresham, University of North Carolina at Greensboro, Greensboro, NC
Complex biological and environmental samples demand high resolution separations techniques for the unique determination of each component. In capillary electrochromatography, a stationary phase is incorporated into the fused silica capillary by one of the following strategies: trapping a particulate phase between two frits, polymerization of monomers into a porous monolith, or covalent attachment to the capillary wall. Of these strategies, the last provides the easiest route to a chromatographic interaction surface for the analytes of interest and provides a way to decrease peak tailing due to surface silanols. To increase the phase ratio of the capillary columns, the inner surface is often etched—a process which produces radial extensions into the capillary and changes the surface charge density.

The work described in this presentation used etched capillaries with a biphenyl stationary phases, some of which display liquid crystalline behavior in the bulk. While biphenyl phases, some displaying liquid crystalline behavior, have been widely studied in gas chromatography, few studies have used them in conjunction with liquid mobile phases. The biphenyl moiety was covalently attached to the capillary wall, and the columns were used to analyze mixtures of pharmaceuticals, proteins, amino acids and

pharmaceuticals. Mixtures of pharmaceuticals, derivatized amino acids and proteins were successfully separated, and the temperature dependent resolution of was also examined.