

CHEMISTRY AND CHEMICAL ENGINEERING

THURSDAY MORNING Lakeview 2

Session 1

Chair: Dr. Karl J. Wallace

8:50 Introduction and Welcome

O3.01

9:00 A NEW ELECTROGENERATED CHEMILUMINESCENT IMMUNOSENSING SYSTEM FOR DETECTION OF C-REACTIVE PROTEIN

Thomas Maestri, Shijun Wang, Wujian Miao
University of Southern Mississippi

Anodic electrogenerated chemiluminescence (ECL) with tri-n-propylamine (TPRA) as a coreactant was used to determine C-reactive protein (CRP) by immobilization on aldehyde-activated US450 paper membrane using tris(2,2'-bipyridyl) ruthenium (II) (Ru(bpy)₃²⁺) labels in a sandwich-type antibody-antigen system. Binding of the anti-CRP protein to the membrane occurred by forming a weakly-bonded Schiff base at the N-terminus of the protein. In order to form a stable bond to membrane, the protein was reduced to a secondary amine with a NaCNBH₃ reducing agent. To detect and enhance the amount of binding of the protein to the membrane, FTIR spectra of several membranes were collected to determine that the greatest amount of binding to the surface occurred after reduction in a slightly basic (pH 9.5) buffer solution. To determine the amount of binding to the membrane, the ratio of the protein peak (~1638 cm⁻¹) to the membrane peak (1576 cm⁻¹) was compared. The results showed a 9.2% increase in binding to the membrane of the protein in pH 9.5 sodium borate solution as opposed to a pH 7.5 PBS buffer solution; binding was also 15.7% higher in a membrane where the Schiff base was reduced compared to one that remained unreduced. ECL detection of CRP through the sandwich-type system was found at an intensity of 0.6 nA for a 1.0 μL solution of CRP. Future work will be to find a linear increase in ECL intensity to CRP concentration.

O3.02

9:20 DETERMINATION OF HEAVY METALS IN WATER SAMPLES BY ICP-AES USING YEAST (*Yamadazyma spartinae*) IMMOBILIZED ON Al₂O₃ NANOPARTICLES

Sitki Baytak², Zikri Arslan¹

¹Jackson State University, ²Nevsehir University, Nevsehir, Turkey

Microorganisms, including yeast, bacteria and

fungi immobilized enable extraction of trace metals from numerous samples when immobilized on natural and synthetic support materials. The process involves a combination of active and passive transport mechanisms, and are generally classified into two divisions as biosorptive (passive) uptake by non-living biomass and bioaccumulation by living cells. Here, a solid phase extraction procedure based on biosorption of Co, Cu, Fe, Mn and Zn on yeast (*Y. spartinae*) loaded on a solid phase of Al₂O₃ nanoparticles. Column contained 100 mg of nano Al₂O₃ with average particle size of 50 nm. Determinations were made by ICP-AES. The conditions including pH, solid-phase mass, flow rates, eluent type and sample volume were examined for the quantitative recovery. Cu and Fe were retained at pH 6 while Co, Mn and Zn were retained at pH 8. Elution was performed with 2 mL of 5% HNO₃. The recoveries of Co, Cu, Fe, Mn and Zn were 100 ± 2%, 98 ± 2%, 100 ± 2%, 98 ± 2% and 99 ± 2%, respectively for spiked water samples. The enrichment factor when using a sample volume of 500 mL was 250 for all metal ions. The detection limits for Co, Cu, Fe, Mn and Zn were 1.4, 1.6, 0.6, 1.3 and 0.6 ng/mL before enrichment respectively. The method was validated by analysis of the standard reference material of water and then applied to tap water and lake water samples.

O3.03

9:40 ELECTRONIC PROPERTIES OF SQUARINE DYES

Thomas Grant White, Karl J. Wallace
University of Southern Mississippi

The coordination chemistry of heavy metals, for example, Fe³⁺, Pb²⁺, Cd²⁺, Hg²⁺, and Zn²⁺, is of current interest, in part, because of their hazards and toxicity in biological, industrial, and agricultural applications. One such dye that has started to appear in the literature is the squaraine class of molecules. These dyes have some unique physical properties. For example, their absorbance typically falls in the visible to NIR region of the spectrum and they also have high extinction coefficients. This property is a very attractive one in sensor design, and is desirable for integration with optical instrumentation. A series of squaraine dyes have been synthesized and their optical properties (UV-VIS and Fluorescence Spectroscopy), and their electrochemical behavior (cyclic voltammetry, and electrogenerated chemiluminescence) has been investigated. The effect of these squaraine dyes towards acid (HCl), base (DBU), and transition metals (for example Fe³⁺, Zn²⁺) will be reported. It has been shown that the dye molecules undergo a structural or conformational change resulting from the respective protonation, deprotonation, or transition metal chelation. The electronic properties of these unique chromophores will be discussed.

O3.04

10:00 FUNDAMENTAL THERMOCHEMICAL PROPERTIES OF AMINO ACIDS: GAS PHASE HEATS OF FORMATION AND ACIDITIES

Michele Stover¹, David Dixon², Virgil Jackson², Myrna Matus²

¹William Carey University, ²University of Alabama

Building on prior work on glycine, glutamic acid, and aspartic acid^{1,2}, the goal of the current work is to provide reliable thermodynamic values for amino acids. The gas phase acidity is the free energy ΔG_{acid} for the reaction

$\text{AH} \rightarrow \text{A}^- + \text{H}^+$. The acidities of the remaining amino acids including histidine, leucine, lysine, methionine, phenylalanine, tryptophan, tyrosine, serine, and valine have been predicted using high level electronic structure theory at the composite G3(MP2) level. A broad range of structures of the neutral compounds were studied to determine the lowest energy conformer with the strongest hydrogen bonding. Anions were created by removing protons at different sites including the important $-\text{CO}_2\text{H}$ and NH groups. The calculated gas-phase acidities (GA =) were obtained by using molecular orbital theory at the G3(MP2) level and density functional theory at the B3LYP/DZVP2 level. Hydrogen bonding plays an important role in the acidities. The heats of formation of the neutral compounds were calculated from atomization energies and isodesmic reactions to provide the first reliable set of thermodynamic properties of the amino acids in the gas phase.

1. "Electronic structure and bonding of the amino acids containing first row atoms." Dixon, D. A.; Lipscomb, W. N. *J. Biol. Chem.* 251, 5992-6000 (1976).

2. "Comprehensive Density Functional Theory Study on Serine and Related Ions in Gas Phase: Conformations, Gas Phase Basicities, and Acidities", Miao, R., Jin, C., Yang, G., Gong, J., Zhao, C., and Zhu, L. *J. Phys. Chem. A*, 109 (10), 2340-2349 (2005).

O3.05

10:20 SELECTIVE DETECTION OF TRIACETONE TRIPEROXIDE USING ELECTROGENERATED CHEMILUMINESCENCE

Suman Parajuli, Wujian Miao

University of Southern Mississippi

The electrogenerated chemiluminescent (ECL) route of detection of triacetone triperoxide (TATP) involves hydrogen peroxide formation which on reduction produces hydroxyl radicals. This radical is a very strong oxidant and can react with $\text{Ru}(\text{bpy})_3^+$ (formed at the electrode by electrochemical reduction) to generate the excited state $\text{Ru}(\text{bpy})_3^{2+*}$ that emits light. The potential source of hydrogen peroxide is the cleaning detergent which could give false positive result for the detection of TATP. The catalase enzyme could decompose H_2O_2 from the sample and avoids false positive results making it possible to detect TATP selectively in the presence of trace amounts of H_2O_2 . Also TATP could be selectively detected in the other common peroxide-based explosives (e.g., hexamethylene

triperoxidediamine, HMTD) with ECL as TATP produces light upon the cathodic scanning whereas HMTD can produce light upon either the anodic potential scanning or cathodic potential scanning.

10:40 Break

Session II

Chair: Dr. Ramaiyer Venkatraman

O3.06

10:50 SYNTHESIS, CHARACTERIZATION, AND ELECTROCATALYTIC ACTIVITY OF NOVEL RUTHENIUM(II)-CONTAINING HYDROGEN PRODUCING PHOTOCATALYSTS.

Nerissa Lewis¹, Toyketa Horne², Dorothy Horton¹, Jason Olaivar¹, Alvin Holder¹, David Tiede³

¹University of Southern Mississippi, ²Alcorn State University, ³Argonne National Laboratory

The main theme in this project was to develop and test the hydrogen-producing capacity of some novel complexes that bear a photosensitizer (a ruthenium(II) metal center) and a catalytic metal center {Co(II) or Ni(II)}, all in one molecule.

Several novel complexes bearing mixed-metal centers were synthesized and characterized. Two reactions between $[\text{Ru}(\text{pbt})_2(\text{L-pyr})](\text{PF}_6)_2$ (where $\text{pbt} = 2\text{-(pyridine-2yl)bezo[d]thiazole}$ and $\text{L-pyr} = 2\text{-pyridin-4-yl-1-oxa-3,7,8-triaza-cyclopenta[1]phenan-threne}$) and $[\text{Ni}_2(\text{dmgBF}_2)_4]$ (where $\text{dmgBF}_2 = \text{difluoroborondimethylglyoximate}$) produced mixed-metal complexes with ruthenium(II) and nickel(II) metal centers in good yields.

The reaction between $[\text{Ru}(\text{N-N})_2(\text{L-pyr})](\text{PF}_6)_2$ (where $\text{N-N} = 1,10\text{-phenanthroline}$, $4,4'\text{-dimethyl-2,2'-bipyridine}$, and $2\text{-(pyridine-2yl)bezo[d]thiazole}$ (pbt); and $\text{L-pyr} = 2\text{-pyridin-4-yl-1-oxa-3,7,8-triaza-cyclopenta[1]phenanthrene}$) and $[\text{Co}(\text{dmgBF}_2)_2(\text{OH}_2)_2]$ produced mixed-metal complexes with ruthenium(II) and cobalt(II) metal centers, viz., $[\text{Ru}(\text{N-N})_2(\text{L-pyr})\text{Co}(\text{dmgBF}_2)_2(\text{OH}_2)](\text{PF}_6)_2$ in good yields.

All complexes were characterized by UV-visible, ^1H NMR, and EPR spectroscopy, and cyclic voltammetry, where appropriate. Cyclic voltammograms with acetonitrile as a solvent exhibited reversible waves for the redox processes, $\text{M}^{\text{II/I}}$ and $\text{M}^{\text{I/0}}$ (where $\text{M} = \text{Co}$ or Ni) for all complexes. In the presence of the $p\text{-cyanoanilinium}$ cation (as a source of H^+ ions), $[\text{Ru}(\text{pbt})_2(\text{L-pyr})\text{Co}(\text{dmgBF}_2)_2(\text{OH}_2)](\text{PF}_6)_2$ and $[\text{Ru}(\text{pbt})_2(\text{L-pyr})\text{Ni}(\text{dmgBF}_2)_2](\text{PF}_6)_2$, induced

electrocatalysis of H^+ ions during a cyclic voltammetric process to generate hydrogen gas in the acetonitrile. From these results, it can be concluded that these mixed-metal complexes have potential to be efficient

photocatalysts which will be used to produce hydrogen from water on irradiation of these complexes in the presence of H^+ ions in aqueous solution.

O3.07

11:10 SPECIATION OF MERCURY IN FISH OTOLITHS BY COLD VAPOR GENERATION ATOMIC ABSORPTION SPECTROSCOPY

Erdal Kenduzler², Melanie McHenry¹, Zikri Arslan¹

¹Jackson State University, ²Mehmet Akif Ersoy University, Burdur, Turkey

Fish otoliths are composed of mainly calcium carbonate that deposit in layers on protein matrix. The trace elements originating from the water of the fish's environment accumulate in the otoliths throughout the life of fish. The elemental signatures of these elements are used as powerful tools in fishery to understand population dynamics, mixing issues and to identify essential nurseries. Mercury has not been utilized yet in such studies due to the detection problems at low levels. It is however known that inorganic Hg accumulates in fish to substantial levels and methylated within the tissues. To date there is no information about the levels of Hg and mercury species in the otoliths of fish. In this study we developed a methodology to achieve identification and quantification Hg species in otoliths to elucidate possible pathways of incorporation of this element. Cold vapor generation has been used as a highly sensitive technique for detection. The conditions for selective generation of Hg vapor from inorganic Hg and methyl Hg were optimized in HCl medium. The effects of various oxidizing agents, including potassium ferricyanide, potassium permanganate, cerium nitrate, were used to convert CH_3HgCl to inorganic Hg. The latter afforded rapid conversion of CH_3HgCl to Hg^{2+} .

Stannous chloride allowed reduction of Hg^{2+} to Hg vapor while $NaBH_4$ was essential in reduction of species from methyl Hg. Under the optimum conditions, the detection limits were around 40 ng/L Hg. Preliminary results indicated that Hg was mainly in methylated form in the otoliths.

O3.08

11:30 N-SUBSTITUTED 1,8-NAPHTHALIMIDES AS FLUORESCENCE PROBES

Wolfgang Kramer, Irene Corrao, Anna Allred, Jeral Self
Millsaps College

Naphthalenediimide derivatives have been of interest due to their fluorescent and DNA intercalating properties. Naphthalimides have also been evaluated for photodynamic therapy but high cytotoxicity posed a problem in phase I and phase II trials.

Phenyl substituted 1,8-naphthalimides have a fluorescence quantum yield of 0.3. The fluorescence is strongly depending on the solvent. Polar protic solvents lower the ISC rate by raising the energy of the second excited triplet state and

lowering the energy of the first excited singlet state. The fluorescence quantum yield consequently increases dramatically.

Substitution with electron donors can result in fluorescence quenching by electron transfer. Aliphatic amines have been used to as pH-dependent fluorescence quencher. In addition, anion binding moieties have been used to create INH-logic gates in combination with amines.

In our studies with nitrogen onium salts we have investigated the influence of aromatic amines with variable spacers and different oxidation potentials. Pyridines were connected to the naphthalimide nitrogen via methylene spacers. The pyridine substitution pattern does strongly influence the naphthalimide. N-oxidation converts pyridine into its electron-rich N-oxide which much more efficiently quenches the naphthalimide fluorescence. N-alkylation reduced the electron density and thus increases fluorescence.

This talk describes the fluorescence changes of 1,8-naphthalimide linked pyridines in different environments as well as their use as fluorescence probes responsive to pH and oxidation state.

11:50 Lunch

THURSDAY AFTERNOON Lakeview 2

Symposium: Chemicals in the Environment, Sensing and Remediation

Chair Dr. Karl J. Wallace

O3.09

1:30 BINDING AND SELECTIVITY ASPECTS OF ANIONS WITH SYNTHETIC RECEPTORS

Md. Alamgir Hossain

Jackson State University

The field of anion coordination chemistry emerged in 1968 with the discovery of diazabicyclic compounds, known as katapinands, by Park and Simmons [1]. These compounds were shown to form inclusion complexes with halide anions by hydrogen bonding interactions in acidic solution, which was later confirmed by X-ray structure determination [2]. During the last two decades, this area has been progressed significantly, and a variety of synthetic receptors have been reported that show high binding affinity and selectivity for common inorganic anions. Among the different classes of anion receptors, polyaza macrocycles are widely investigated systems for the binding of a variety of anions in both solution and solid states[3]. The protonation ability of amino groups makes them effective for anion binding through hydrogen bonding interactions. In an attempt to synthesize selective anion receptor for environmentally important anions, we synthesized both macrocyclic and macrobicyclic compounds from the schiff's base condensation of amines and corresponding aldehyde followed by sodium borohydride reduction. The synthesized receptors have been studied for both halide and oxoanions

in both solution and solid states. Details of the synthetic procedures, NMR binding studies, and solid state structures will be discussed in this talk. References: [1]. Park, C. H.; Simmons, H. E. J. Am. Chem. Soc. 1968, 90, 2431. [2]. Bell, R. A.; Christoph, G. G.; Fronczek, F. R.; Marsh, R. E. Science, 1975, 190, [3]. Hossain, M. A. Curr. Org. Chem., 2008, 12, 1231.

O3.10

2:15 DEVELOPMENT OF A NEXT GENERATION SENSOR FOR MEASURING BIOLOGICALLY AVAILABLE IRON IN SEAWATER

Karen Orcutt¹, Karl Wallace¹, Mark Wells¹

¹University of Southern Mississippi, ²University of Maine

There is increasing evidence that iron is important not only in the regulation of bulk phytoplankton production in large regions of the world oceans, but that it also profoundly influences the speciation of algae within the phytoplankton assemblage. The broad implications resulting from these dual effects range from impacts on the global carbon cycle to the possible stimulation of harmful algal blooms. There is a strong need for ultra-sensitive, real-time monitoring and detection technologies that capture the reactive iron pool in seawater that is available to eukaryotic phytoplankton. We present preliminary work on the development of a novel photoactive nanosensor to measure the chemically reactive iron in seawater that builds on our previous work using a liposome-based nanodevice. The nanosensor will be based on Probes Encapsulated by Biologically Localized Embedding (PEBBLE) technology. This approach uses a combination of Time Resolved fluorescence (TRF) and Fluorescence Resonance Energy Transfer (FRET) to greatly amplify the signal to achieve the picomolar level sensitivity needed to study iron in both coastal and offshore waters.

3:00 Break

O3.11

3:15 MOLECULAR GOLD NANOCCLUSERS: ATOM BY ATOM DESIGN

Amala Dass

University of Mississippi

Molecular gold nanoclusters such as Au₂₅(SR)₁₈, Au₃₈(SR)₂₄, Au₆₈(SR)₃₄, Au₁₀₂(SR)₄₄ and Au₁₄₄(SR)₆₀ contain a distinct number of core gold atoms and surface thiolate ligands. Synthesis, spectroscopic and mass spectrometric characterizations (MALDI-MS and ESI-MS) of these nanoclusters will be discussed. The specific topics include a) mass spectrometric identification of Au₆₈(SR)₃₄; (b) Size evolution in Au₂₅ synthesis; and (c) geometric stability of molecular gold nanoclusters.

O3.12

4:00 MEMS CHEMICAPACITIVE CHEMICAL SENSOR SYSTEMS

Todd Mlsna

Mississippi State University

We have been developing chemical sensors that use polymer filled micromachined capacitors to measure the dielectric constant of an array of selectively absorbing materials. Capable of detecting vapors of organic compounds and inorganic gases, each device has ten sensors on a single chip, with different coatings for redundancy and interferent rejection. We have developed MEMS sensors for gas-phase analytes including volatile organic compounds (VOCs), chemical warfare agents (CWA), toxic industrial chemicals and materials (TICS & TIMS), emission gases and hydrogen. The compact size, low power consumption, and low cost of these sensors make them ideal for integration into varied packages for numerous applications. Portable sensor and chemical separation systems are needed for defense and civilian monitoring applications. With recent advances in microfabrication, these systems have achieved capabilities comparable to analytical equipment in laboratories for some applications. We have developed and tested several prototypes that utilize our MEMS sensors with varied configurations. Our most advanced is a miniature gas chromatograph that is compatible with the restrictive size, power and weight limits needed for use in the field or in many industrial monitoring situations. This system can operate with multiple detectors including our polymer-filled, micromachined capacitors. In front of the detector we have built a device containing an air or liquid injection sampling mechanism, a chemical preconcentrator and a chromatographic capillary column. This small system is capable of separating and detecting many target analytes such as common volatile organic compounds, solvents and chemical warfare agents.

4:45 Closing Remarks

THURSDAY EVENING

Dodgen Poster Session

Exhibit Hall C

Posters on display, 6:00p – 7:00p

Posters must be put up between 4:30p – 5:00p

P3.01

XRF ANALYSIS OF RUBBER PIGMENT ASH USING COMPTON SCATTER MATRIX ABSORPTION CORRECTIONS

Charles Smithhart, Linsey Giachelli

Delta State University

Ash samples were obtained from twenty-four commercial rubber pigment additive packages using an ASTM procedure. XRF spectra of the ashes were collected using a Spectrace 5000 EDXRF spectrometer equipped with a rhodium target X-ray tube. Two NIST standard reference materials were analyzed under the same conditions for calibration and control purposes. Semi-quantitative

elemental abundances were obtained by comparing the measured Rayleigh /Compton peak intensity ratios from the ashes to those of one NIST standard. Using another NIST SRM as a control, the results indicated that this method is suitable for quick and accurate semi-quantitative analyses of rubber pigment ash as long as considerations are made for absorption edge effects.

P3.02 EXPRESSION AND CHARACTERIZATION OF RECOMBINANT HUMAN GRANULIN-A (hGrn A) AND ITS POTENTIAL INTERACTIONS WITH AMYLOID- β (A β) PEPTIDE IN ALZHEIMER'S DISEASE.

Michael Samel¹, Amit Kumar¹, Andrew Bateman², Vijay Rangachari¹

¹University of Southern Mississippi, ²McGill University, Montreal, Quebec, Canada

Granulins (Grn) are generated by the elastase cleavage from its larger, ubiquitously expressed precursor, progranulin (PGrn) that has recently been understood to play a role in frontotemporal dementia (FTD). Several lines of evidence seem to suggest a potential interaction between PGrn/Grn with amyloid- β (Ab), however, this has never gained significant attention among the neuroscience community. It is interesting to know that expression levels of PGrn (and Grn) are increased in many neurodegenerative diseases such as Alzheimer's (AD), Parkinson's (PD) and Creutzfeldt-Jakob disease and ALS. It is also noteworthy that PGrns are observed to be associated with microglia surrounding Ab plaques in AD. Since its involvement in neurodegenerative diseases was established in early 2006, PGrn/Grn has gained significant attention in the neuroscience community. However, since their roles in neurodegenerative diseases have only started to emerge, not much is known about their biochemical functions and molecular mechanisms in relation to AD. Based on the structural homology and BLAST structure comparisons between Grns and Ab fibrils, we hypothesize that Grn can potentially interact with Ab either by nucleation or by inhibition. Here we present the expression of human Grn-A (hGrnA) in E coli, along with purification and characterization of the protein by various biochemical and biophysical methods. The next step would be to characterize the interactions between Ab and hGrnA mainly by fluorescence techniques. Understanding the interactions between these two proteins may provide new insights into AD from an entirely new perspective.

P3.03 PREPARATION OF UNNATURAL AMINO ACIDS USING β -LACTONE INTERMEDIATES

Emily Vogel, Douglas Masterson
University of Southern Mississippi

α -Methyl amino acids have received considerable attention in recent years due to their versatility. We have developed methods, both enzymatic and chemical, which

allow us to prepare a series of unnatural amino acids from a common synthetic intermediate. However, we have tried to prepare phenylalanine and tyrosine analogues using this techniques with mixed success. We have utilized a β -lactone intermediate to overcome this problem. The β -lactone allows us to insert the side chain of either tyrosine or phenylalanine using straightforward methods with reasonable yield.

P3.04 SYNTHESIS AND CHARACTERIZATION OF 2- HYDROXY BENZALDEHYDE-N-4, 4'-DIMETHYL-3- THIOSEMICARBAZONE AND ITS COPPER(II) COMPLEX

Ameera Haamid¹, Ramaiyer Venkatraman¹, Frank Fronczek²

¹Jackson State University, ²Louisiana State University

Thiosemicarbazones exhibit interesting biological properties. In solution, thiosemicarbazone molecules can exist in thione–thiol tautomeric form. This unique property of thiosemicarbazone is not only the presence of many electron donor centers in the structure but also the bonding characteristics. As a ligand, thiosemicarbazones are well known to behave as chelating agents towards a wide range of metallic ions forming structurally different complexes. In many instances, they bind the metal ions through the hydrazinic nitrogen, thione sulfur atom and oxygen or nitrogen from parent ketone or aldehyde. Among the metal ions that complex with thiosemicarbazones, copper complexes are of prime interest due to their enhanced and proven biological activity in the field of medicine, industrial and agriculture. In this research, we report the synthesis, crystal structure and spectral data of the title ligand (**1**), C₁₀H₁₃N₃OS, and the copper (II) complex (**2**), C₂₀H₂₂Cu₂N₆O₂S₂. The copper (II) complex is prepared by using 1:1 metal-to-ligand reactant. The metal complex is a dimer in the solid state. The copper atoms are bridged by the phenolic oxygen and in addition are coordinated through the thione sulfur and hydrazinic nitrogen of the thiosemicarbazone molecule exhibiting a square planar geometry around the copper atom. The crystal data is supported by NMR and IR spectroscopy. (Supported by the National Science Foundation under CHE-082135)

P3.05 SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF CYCLOPENTANONE THIOSEMICARBAZONES

Haamid Ameera¹, Ramaiyer Venkatraman¹, Lee Ken. S¹, Valente Edward. J²

¹Jackson State University, ²University of Portland

Thiosemicarbazones and their metal complexes have been studied for their potential biological activity. The anti-neoplastic activity of thiosemicarbazones has distinct

structure-activity relationships among their substituted derivatives. In our continuing work with thiosemicarbazones, and their derivatives, we synthesized relatively three thiosemicarbazones of cyclopentanone. (1) Syn, 1E-4Z-cyclopentano-4-methyl-3-thiosemicarbazone, C₇H₁₃N₃S. Single molecules of (1) comprise the asymmetric unit, two in the cell. Molecules form dimeric H-bonds with neighbors linking molecules in pairs with R₂²(8) patterns. (2) 2-(dimethylamino)-5-(2'-cyclopentano-hydrazo)-1,3,4-thiadiazole, C₆H₁₅N₃S. The molecule is a spiro thiosemicarbazone, with the ipso carbon of cyclopentyl ring making two bonds to the terminal thiosemicarbazone nitrogens. Molecules are linked in pairs by complementary H-bonding from N4-H...S, forming R₂²(10) patterns; the N-H...S angle is 166.0°. The amine is non-planar. (3) 1,2,4-triazospiro[4.4]nonan-3-thione, C₉H₁₅N₃S. Single molecules comprise the asymmetric unit, four in the unit cell. The molecule shows the unexpected diazothiolane ring, indicating that a second condensation in an attempt to form the thiosemicarbazone of cyclopentanone. Hydrogen bonding links molecules into dimers through N-H...N contacts. (Supported by the National Science Foundation under CHE-0821357)

P3.06

EFFECTS OF FATTY ACIDS AND PHOSPHOLIPIDS ON AMYLOID-β (Aβ) PEPTIDE AGGREGATION.

Amit Kumar, Rebekah Rice, Shiela A. Lidell, Pritesh S. Patel, Dipti Singh, Lea C. Paslay, Sara Morgan, Vijay Rangachari

University Southern Mississippi

The aggregates of Aβ found in brains of Alzheimer's patients are strongly believed to be the cause for neuronal death and cognitive decline. Among the different forms of Aβ aggregates, smaller aggregates called 'soluble oligomers' are increasingly believed to be the primary neurotoxic species responsible for early synaptic dysfunction. Since it is well known that the Aβ aggregation is a nucleation dependant process, it is widely believed that the toxic oligomers are intermediates to fibril formation, or what we call the 'on-pathway' products. Although it is true that there may be toxic oligomers along the fibril formation pathway, it is not obligatory that all toxic oligomers must be 'on-pathway' intermediates. It is important to understand the pathways because if the oligomers are 'off-pathway' products, their half-life can be significantly longer than the 'on-pathway' ones that may result in prolonged toxicity to the neuronal cells. Here, we test this hypothesis in the presence of saturated fatty acids and phosphatidylglycerol lipids by varying their carbon chain lengths. We observed that Aβ aggregation can adopt more than one pathway, and the pathway is dictated by Aβ-fatty acid/lipid ratio. Oligomers generated from lipids and fatty acids were isolated and characterized using thioflavin-T (ThT) fluorescence, immunoblotting and atomic force microscopy (AFM). These data are presented and discussed.

P3.07

TRAPPING OF METHANOL BY POLYAZA CRYPTAND

Musabbir Saeed¹, Ganna Gryn'ova¹, Douglas Powell², Jerzy Leszczynski¹, Md. Alamgir Hossain¹
¹Jackson State University, ²University of Oklahoma

The recognition of neutral species is one of the challenges in the field of host guest chemistry. The design of receptors capable of binding neutral molecules is gaining considerable attention, because for their potential applications in separation chemistry. Synthetic receptors can be used to bind and to monitor neutral molecules. Although there are considerable progresses in binding of charged species, however, only a few synthetic receptors have been reported that selectively bind neutral molecule. Polyazamacrocycles are synthesized from the corresponding amines and dialdehyde under high dilution condition followed by reduction. These compounds are potential hosts for anions when they are protonated, and can interact with anions by electrostatic and hydrogen bonding interactions. However, we isolated a crystal of sulfate complex with p-xylyl cryptand showing a methanol molecule inside the cavity. The three sulfates however are cleft between the macrocyclic arms. To our knowledge, this is the first crystallographic evidence with encapsulated methanol. We also have investigated the interactions in obtained complex of methanol by the means of quantum Mechanical calculation (B3LYP/6-31G(d) level of theory). Calculated energy of interaction between methanol and scavenger molecule is -15.9 kcal/mol, which denotes the stabilization of the system through the formation of a complex. We have also analyzed forming bonding interactions in terms of Bader's "atoms in molecules" theory. Weak interactions of several types (hydrogen, dihydrogen, Van der Waals and weak covalent bonding) are observed in formed complex due to the values of electron densities and Laplacians of the electron densities at bond critical points.

P3.08

SYNTHESIS OF HEXAAZAMACRYOCYCLE FOR ANION BINDING

John S. mendy¹, Kalpana Rani Dey¹, Musabbir A. Saeed¹, Frank R. Fronczek¹, Alamgir Hossain¹
¹Jackson state University, ²Louisiana State University

Although the majority of enzymatic reactions is associated with anions, the field of anion coordination chemistry is less explored area as compared to the field of cation coordination chemistry. In an attempt to design selective anion receptors, we prepared a hexamine macrocycle from the high dilution condensation of m-xylyl dicarboxaldehyde and N-(2-aminoethyl) ethane-1,2 diamine, followed by the diborane reduction. The ligand has been characterized and studied for halides and oxoanions in both solution and solid states. During this work, several

anion complexes have been structurally characterized by X-ray analysis. Details of the synthesis, NMR titration studies, and crystal structures will be presented in this poster.

P3.09

RATIONAL DESIGN OF ANION SENSORS: SYNTHESIS AND BINDING OF INORGANIC ANIONS IN LIPOPHILIC SOLVENTS

Kalpana Rani Dey, Toyketa Horne, Md. Alamgir Hossain
Jackson State University

The anion sensor chemistry is one of the important areas in molecular recognition. As compared to the cation sensors, the ligands for anion sensing are still in infancy in the literature even though anions play an important role in biology, chemistry and environment. The majority of enzyme substrates and co-factors are anionic species. It is known that an excess amount of phosphate and nitrate can lead to eutrophication, as well as to disrupt aquatic life cycles. Some other anions, like perchlorate and perchlorate have an adverse effect on the environment, and causes pollution. The development of the synthetic chemosensors is of particular interest in sensing chemistry, because of their high selectivity, sensitivity, and simplicity. During the course of our study, we developed new fluorescent sensors based on the introduction of dansyl groups to acyclic and cyclic polyamines. After protonation of the unattached amines, the ligands were found to interact with both halides and oxoanions in lipophilic solvents. The sensing ability of the synthesized ligands has been studied by fluorescence titration method. The results demonstrate that the receptor exhibits strong selectivity for iodide and phosphate over other anions. The details of the solution studies will be focused in the presentation.

P3.10

TRIPODAL BASED HOSTS FOR ANION BINDING

Whitney Quinn, Brittany Musabbir Saeed, Md. Alamgir Hossain

Mississippi State University

Anions play a significant role in chemistry and biology. Simple inorganic anions like halides and oxoanions are harmful and can have adverse effects in the human body if present in excess amounts [1]. For example, phosphate, nitrate, sulfate, and perchlorate are the major contaminants in soil and water. It has been reported that arsenate and fluoride are presently abundant in ground water that causes severe health problems. Synthetic hosts can be used to bind and eliminate these anionic pollutants. Tris(aminoethyl)-amine, tren (L1) with C₃ symmetry is often used to build azacryptands with amine or amide functionality. These molecules are of particular interest for binding anions with three-fold rotation axes, such as nitrate, phosphate, perchlorate and sulfate. The binding predominantly occurs through hydrogen bonding and electrostatic interactions of tren nitrogens with negatively charged species. During the course of our work, we isolated the complexes of TREN with sulfate and perchlorate. The tren was further modified

with anthracene units to get the desired host. Details of solid and NMR binding studies will be included in this poster.

P3.11

SELECTIVE COLORIMETRIC AND HIGHLY SENSITIVE DYNAMIC LIGHT SCATTERING ASSAY FOR ARSENIC DETECTION USING GOLD NANOPARTICLE

Sadia Khan, Jhansi Kalluri, Tahir Arbneshi, Adria Neely, Perry Candice, Paresh Ray
Jackson State University

Arsenic contaminated drinking water poses a threat to global health. Worldwide nearly 140 million people may have been exposed to drinking water with arsenic contamination levels higher than the WHO guidelines of 10ppb. Unlike organic pollutants, arsenic cannot be transformed into a non-toxic material, as a result there is a long-term need for regular monitoring at sites where it occurs naturally at elevated concentrations. Current laboratory based analytical procedure is less sensitive, time consuming and it needs a series of enrichment steps. Though electrochemical methods suitable for the development of low cost hand-held test instruments, but it has been hampered due to lack of selectivity against other contaminants e.g. lead, copper, zinc, iron, and mercury in water samples. As a result, the development of ultrasensitive assays for the real-time detection of arsenic has attracted considerable research efforts in recent years. In last 15 years, noble metal nanostructures attract much interest because of their unique optical properties, including large optical field enhancements resulting in the scattering and absorption of light. Very recently, Surface Enhanced Raman Scattering (SERS) based assay and Surface Plasmon Resonance (SPR) sensor has been reported for Arsenic detection till 1ppb, but none of these assays shows selectivity against alkali, alkaline earth and transition heavy metal ions, which is a must for real life application, in environmental samples. Driven by the need, we use glutathione, dithiothreitol and cysteine modified gold nanoparticle based Dynamic Light Scattering probe for label free detection of Arsenic, with excellent detection limit (10ppt) and selectivity over other analytes.

P3.12

SOLID PHASE PRECONCENTRATION ON ACTIVATED ALUMINA WITH EDTA FOR DETERMINATION OF TRACE ELEMENTS IN FISH OTOLITHS BY ICP-AES

Fahmida Zereen¹, Sitki Baytak², Zikri Arslan¹

¹*Jackson State University*, ²*Nevsehir University, Nevsehir, Turkey*

The use of solid phase extraction or preconcentration protocols has afforded powerful tools to environmental chemists for determination of trace elements and heavy metals at sub-ppb levels from various matrices. To date different adsorbents, including silica gel, activated carbon, amberlite resins, ambersorb, pumice stone and alumina have been used as a solid support material. In this

study, a procedure for the determination of trace and toxic metals has been described by ICP-AES based on retention of EDTA complexes on a minicolumn packed with activated alumina. Optimum conditions for pH, amount of adsorbent, eluent solution and flow rate have been determined for quantitative preconcentration of the elements. All elements were retained on the column between pH 2 and 4 followed by elution with 5 mL of 5% HNO₃ solution. The recoveries for Cd, Co, Cu, Fe, Mn, Ni, Pb, V and Zn varied between 95 and 100%. Enrichment factors varied from 200-fold for Cu, Fe, Ni and Pb, 150-fold for Cd, Co, V, Zn 150 to 50-fold for Mn. The preconcentration method allowed detection limits to be improved at least by factor of ten for the elements of interest. The proposed procedure was applied for the determination of the elements in water and fish otoliths by ICP-AES.

P3.13 SOLID PHASE PRECONCENTRATION OF ARSENIC AND ANTIMONY FOR DETERMINATION BY HYDRIDE GENERATION ICP-AES

Zikri Arslan¹, Sitki Baytak², Musabbir Saeed¹, Alamgir Hossain¹

¹Jackson State University, Jackson, ²Nevsehir University, Nevsehir, Turkey

Accurate measurement of arsenic levels in water and other environmental samples is important for public health and protection. In this study, we utilized a novel para-xylyl cryptard-base (PEACRYT) chelating agent that exhibit strong tendency to form a complex with arsenic and antimony within acidic range in water samples. For instrumental analysis, arsenic and antimony complexes were preconcentrated on a minicolumn of activated alumina. The retention of As and Sb occurred within a pH range from pH 4 to 6. The species retained on the column were collected into 15-mL tubes with 10 mL of 50% HNO₃ solution. A hydride generation approach was used to further improve the sensitivity of As and Sb in determination by ICP-AES. Experimental conditions of on-line hydride generation system were optimized for acidity of sample and reductant (NaBH₄) concentration. Practically, 1% HCl and 1% NaBH₄ medium was sufficient for generation of AsH₃ and SbH₃. L-cysteine substantially increased the signals at a concentration of 1% when added on-line to sample solutions. The same agent has significantly eliminated the interferences of transition metals and other hydride forming elements on As and Sb. The procedure has been applied to the determination of As and Sb in water samples and biological materials

P3.14 MEASUREMENT OF IONIC CADMIUM BY ICP-AES FROM LIVER AND KIDNEY SAMPLES OF RATS EXPOSED TO CDSE NANOPARTICLES

Wanaki McDuffy¹, Sitki Baytak², Zikri Arslan¹

¹Jackson State University, ²Nevsehir University, Nevsehir, Turkey

CdSe nanoparticles mainly accumulate in liver and kidney of rats. It was also found that particles dissociate to ionic Cd²⁺ and Se²⁻ in the organs. This phenomenon elevates the risks associated with exposure to CdSe nanoparticles as ionic Cd is highly toxic. In an attempt to provide conclusive evidence to the presence of ionic Cd²⁺ in the liver and kidney samples of the rats that were exposed to CdSe nanoparticles, we investigated separation of ionic Cd²⁺ from organs of rats without altering nanoparticle composition. Several solvents have been examined to elucidate the stability of CdSe nanoparticles during sonication, including water, ethanol and dilute HCl and HNO₃. Acid concentration in sonication medium was varied from 0.1 to 1%. It was found that QDs aggregate even in 0.1% HCl and HNO₃, but were stable in water and ethanol. Interestingly it was also found that sonication did lead to any significant dissociation of CdSe QDs to ionic Cd²⁺ and Se²⁻ in dilute acids and the aggregated dots were simply separated from the ionic aqueous portion by centrifugation. For organs, 0.1 g portions of liver and kidney were homogenized by sonicating 2 min in 1% HCl medium. Homogenates were centrifuged at 12,000 rpm for 30 min and then aqueous layer was collected. The residual tissue containing the intact QDs was digested in HNO₃. Both portions were analyzed by ICP-AES. Results were compared with those obtained from ICP-MS analysis of the organs to total Cd levels.

P3.15 TRACE METAL PRECONCENTRATION WITH DIPHENYLCARBAZONE IMMOBILIZED ON NANO TiO₂ SOLID SUPPORT FOR DETERMINATION BY ICP-AES

Sitki Baytak², Zikri Arslan¹

¹Jackson State University, ²Nevsehir University, Nevsehir, Turkey

Trace elements such as Co, Cr, Cu, Fe, Mn and Zn are known as essential trace metals for biological organisms. However, high levels of these elements induce toxic effects and therefore, monitoring and determination of these elements are critical for human and environmental health. Solid phase extraction has become popular for determination of trace metals via preconcentration. Applications of various materials have been demonstrated as a solid phase. In this study, a solid phase extraction procedure has been described for the determination of Co, Cr, Cu, Fe, Mn and Zn by ICP-AES using mini-column of diphenylcarbazone (DPC) immobilized on TiO₂ nanoparticles. The retention pH, mass of adsorbent, type of eluent solution and its volume, effect of flow rate and effect of volume samples were optimized. The recoveries of Co,

Cr, Cu, Fe, Mn and Zn under the optimum conditions were $98 \pm 2\%$, $97 \pm 2\%$, $98 \pm 2\%$, $98 \pm 2\%$, $100 \pm 2\%$, and $100 \pm 2\%$, respectively. The preconcentration method was measured by ICP-AES. The detection limits were 1.3, 1.5, 0.7, 1.4, 1.6 and 0.8 ng/mL for Co, Cr, Cu, Fe, Mn and Zn before enrichment respectively. The method was validated by analysis of water and fish reference materials and then applied to the determination of Co, Cr, Cu, Fe, Mn and Zn in water samples by ICP-AES.

P3.16

THE ANALYTICAL METHOD OF MASS SPECTROMETRY AND ITS APPLICATION TO BIOLOGY & POLYMER SCIENCE

Chrys Wesdemiotis¹, Leroy Lucas¹

¹Mississippi Valley State University, ²The University of Akron

Basically, mass spectrometry & its applications in biology and polymer science are showcased in this experiment to determine structural end groups of unknown compounds. Mass spectrometry comes to use when finding advancements in polymers as well as cell organelles like tissue. The MALDI-TOF/TOF is characterized by sample preparation & having a large tolerance to combination by buffers, salts, etc. When preparing the standard, there are three parts: metric, sample, & salt. The given ratio for the metric, sample, & salt is 10:2:1, respectively. In the standard preparation, 20mg/ml of metric (DCTB) was used to dissolve in the solvent (THF) and 10mg/ml of sample (PMMA) was used to dissolve in THF. Lastly, 10mg/ml of salt was used to dissolve in THF. Results come out in the form of distribution trend chart called a spectrum when analyzing data from the Bruker Daltonics Ultraflex MALDI TOF/TOF mass spectrometer. The trend chart of the individual view of the distance between two peaks on the spectrum is called spectra. The repeating number is used to make an accurate guess of what is the end group's molecular weight based on the given weights in the standard. In short, the end groups' molecular weights are pending on the monoisotopic mass. The assumed weight is the same as the repeating number: 100.0524 Da. With this assumption on the monoisotopic mass, there is miniscule proof from the peaks that there is an unknown part in the standard as well as a given structure.

P3.17

SYNTHESIS OF A LIBRARY OF BIFUNCTIONAL DNA-CLEAVING REAGENTS

Brooke Lassiter, GeNita Finley, Sameer Goel, Woods Curry, Wolfgang Kramer
Millsaps College

Nitrogen onium salts based on aromatic heterocycles have a potential as photodynamic therapy drugs. The light-induced homolytical nitrogen-oxygen bond cleavage yields a radical cation of the aromatic heterocycle and an alkoxy radical. Both of these transient species are highly reactive and can induce oxidation reactions (radical

cation) and radical reactions (alkoxy radical). Both of the species are produced with a quantum yield of about 0.6. Energy wasting steps appear to be the geminate pair recombination to form several isomers of the methoxy substituted aromatic heterocycle.

To expand the library of 1,8-naphthalamide linked onium salts we attempt to modify the spacer length as well as the attached aromatic heterocycle. Several synthesis attempts have been made to extend the methylene spacer length. Mitsunobu transformation of alcohols into the phthalimides was interfered by the nucleophilic pyridine nitrogen. Variation of the heterocycle can be accomplished by Friedlaender quinoline synthesis. The precursors were synthesized by Swern oxidation and aniline reduction. After the synthesis, oxidation yielded the heteroaromatic N-oxide which was alkylated by trimethyloxonium tetrafluoroborate to give the photoreactive N-methoxy salt. The isoelectronic, photostable N-ethyl derivative was obtained by direct alkylation of the parent heterocycle. The synthesis and photochemistry of the novel compounds is investigated and discussed.

P3.18

DECARBOXYLATIVE PHOTOCYCLIZATION OF CATIONIC PHTHALIMIDE AND QUINOLINE/ISOQUINOLINE ω -CARBOXYLIC ACIDS

David Sandlin, Eli Smith, Wolfgang Kramer
Millsaps College

The decarboxylative photocyclization is an elegant photochemical way to synthesize small to medium sized heterocycles. The product is a pyrrolizidine annelated structure. Several functional groups are tolerated and ring sizes up to 36 members have been isolated with appropriate precursors. The synthetic potential of the reaction is diminished by the incorporation of the phthalimide nitrogen into the product.

To expand the versatility of the decarboxylative photocyclization we are cationic precursors as well as different chromophors. Cationic precursors will enable us to use chiral biomolecules, such as DNA, as chiral auxiliaries as well as explore potential interactions in the course of the reaction. In one example, the phthalimide chromophor is attached to a nonconjugated pyridinium moiety which carries the positive charge.

The use of different chromophors will greatly increase the synthetic potential of the cyclization reaction. The simple chromophors quinoline, isoquinoline or phenanthridine will give access to new classes of compounds. It has been shown that electron transfer fluorescence quenching does take place in quinoline betaines compounds.

The synthesis of the precursors as well as the photochemical transformation is discussed.

P3.19

SYNTHESIS AND CHARACTERIZATION OF Au₁₄₄ AND Au₂₅ MIXED MONOLAYER NANOPARTICLES

Rebecca Hardy¹, Laurence Angel², Amala Dass¹

¹University of Mississippi, ²Texas A&M University-Commerce

Nanotechnology is a growing field having great influence in healthcare where for instance gold nanoparticles can be used to detect and treat cancer. It is the goal of Au₁₄₄ nanoparticle research to purify the particles to determine the structure so the particular nanoparticle, Au₁₄₄, can be utilized in this respect. A precise method of Au₁₄₄ synthesis has been developed and is being utilized in the lab. UV-Vis and mass spectrometry have proven the synthesis of these nanoparticles from this method. In addition, results from mixed monolayer Au₂₅ particles will also be presented.

P3.20 BIFUNCTIONAL DNA-CLEAVING REAGENTS BASED ON A LIGHT-INDUCED HOMOLYTICAL NITROGEN-OXYGEN BOND CLEAVAGE

Austin Baker, Woods Curry, Ashley Wells, Victoria Purvis, Wolfgang Kramer
Millsaps College

The light-induced homolytic nitrogen-oxygen bond cleavage of N-methoxy nitrogen onium salts produces two transient species, each of which has been shown to damage DNA. Each species is reacting with a different mechanism. While the formed radical cation targets the DNA bases, the methoxy radical damages the DNA backbone via hydrogen abstraction. The efficiency of this reaction has been analyzed by the determination of the quantum yield of ion formation. Each transient species if produced with a yield of about 0.6, the energy wasting step being geminate pair recombination to yield methoxy-substituted heterocycles. To effectively cleave DNA, a high ground-state association is desired. DNA binding is determined by UV/VIS, fluorescence and CD spectroscopy titrations. Interestingly, the changes in the CD spectrum can give information about the binding mode. The influence of the spacer length and the heterocycle is evaluated and the synthesis of bifunctional onium salts is optimized with those results. In vitro DNA cleaving efficiency is determined compared to a known photochemical DNA cleaver by gel electrophoresis with ethidium bromide staining.

P3.21 NANOCLUSTER SIZE EVOLUTION STUDIED BY MASS SPECTROMETRY IN ROOM TEMPERATURE Au₂₅(SR)₁₈ SYNTHESIS

Asantha Dharmaratne¹, Thomas Krick², Amala Dass¹

¹University of Mississippi, ²University of Minnesota

We have carried out a room temperature facile synthesis of Au₂₅(SCH₂CH₂Ph)₁₈. A systematic mass

spectrometric investigation unraveled the underlying size evolution process that yielded a monodisperse Au₂₅. To be more specific, at early stages of the reaction a mixture of Au₂₅, Au₃₈, Au_{~44}, Au₆₈ and Au₁₀₂ is formed and subsequent size evolution have led to the synthesis of highly monodisperse Au₂₅. The size evolution via structural reconstruction of the larger cores such as 38, ~44, 68 and 102 to Au₂₅ nanocluster have also been studied. Having compared the results that we obtained from UV-vis, TEM, TGA or electrochemical measurements, it was revealed that MALDI mass spectrometry is an indispensable tool that probes the mechanism of nanocluster synthesis providing more concrete information.

P3.22 SYNTHESIS AND CHARACTERIZATION OF Au₃₈ NANOPARTICLES

Lance Majors¹, Asantha Dharmaratne¹, Laurence Angel², Amala Dass¹

¹University of Mississippi, ²Texas A&M University - Commerce

It has been a focus of nanoparticle research to determine the structural features and synthesis of the Au₃₈ nanocluster for some time. The complexity of Au₃₈ purification from the commonly used synthesis has been the gap between obtaining the Au₃₈ nanoclusters in its native form and crystallizing it for structural studies. A relatively new method of synthesis of mostly pure Au₃₈ nanoparticles has bridged this gap and brought about new questions concerning reaction conditions on particle formation. Utilizing this new method, the synthesis and purification of Au₃₈ has been verified using UV-vis and mass spectrometric methods. Studies on particle formation have been carried out to further understand kinetics and cluster aggregation during synthesis. The crystallization of the Au₃₈ clusters is an ongoing task in order to determine the structural features of the nanoparticle.

P3.23 REAL TIME FEED BACK CONTROL OF BIOMASS GASIFICATION

Todd Mlsna, Bidhya Kunwar
Mississippi State University

We are working on an ONR sponsored program to optimize the conversion of biomass to biofuel for DOD aviation. The process includes three steps 1) biomass conversion to synthesis gas (carbon monoxide and hydrogen) at high temperature; 2) purification and compression of the synthesis gas and 3) catalytic conversion to aviation fuel. The focus of our work is to develop real time chemical monitoring hardware to track the production and composition of the synthesis gas. We then can use this information in a feedback control loop will to dictate the composition of the synthesis gas through the Water Gas

Shift Reaction.

For this program we are teaming with Seacoast Science, Inc. who has designed, fabricated and completed preliminary field test of an integrated mini gas chromatograph. This system operates using ambient air and thus requires no carrier gas for increased portability. The proposed system will be able to track the concentration of the individual chemicals emitted from bio conversion process. This information is required to optimize the conversion of synthesis gas to aviation fuel. Feedback driven control systems will receive information from the sensor and make decisions regarding heating, venting, air velocity and humidity.

P3.24

GAS CHROMATOGRAPH IN ACADEMIC CHEMISTRY LABORATORIES

Todd Mlsna, Jeannie Kidd
Mississippi State University

Vernier Software and Technology, Inc. is introduced a new sensor instrument, a portable gas chromatograph in August of 2009. The new instrument, the Vernier/Seacoast Science GC is a perfect fit for today's student learning how to use modern instrumentation. Gas chromatography is an analytical technique in widespread use in many of today's high-tech careers. A mixture of chemicals can be loaded onto a gas chromatography unit and separated into its individual components. This separation allows an informed user to identify the individual compounds of a mixture and potentially to recognize what chemicals are present in the sample of interest. Gas chromatography is used in many biotechnology, chemistry and health related careers and exposure to instrumentation of this sort is extremely relevant for students entering these fields. Laboratories for this unit are being developed in our laboratory in collaboration with Dr. Jack Randall at Vernier Software and Technology. Incorporation of this unit into the general chemistry curriculum will focus on Principles of Chromatography in General Chem I, Quantification Studies in General Chem. II, and Reactions for Organic Chemistry. Several new labs will be presented including those that teach the separation and quantification with chromatography, Raoult's Law and oxidation of an alcohol into a ketone along with the concepts that they are designed to teach the student

P3.25

CHARACTERIZATION OF LABORATORY GRADED AEROSOLS GENERATED FROM METERED DOSE AEROSOL GENERATORS

Courtney Johnson, Mohammed Ali
Jackson State University

Characterizing the mechanical properties of aerosol particles is very much useful to understand their effects on environment or administration as pulmonary medicine. Aerosol can be defined as a suspension of solid or liquid particles in a gas. This gaseous substance does not only

pollute environment but also useful as medicine in the treatment of respiratory illness like asthma. The electromechanical methods that govern the fate of aerosols in the environment or human lung are impaction, gravitational settling, Brownian diffusion, interception, and electrostatic force. Understanding these deposition methods require precise quantification and analysis of aerosol particle's size, which is referred as aerodynamic diameter in the literature. In this study we present the method of characterization and analysis of this vital mechanical property. Laboratory graded aerosols were generated from commercially available metered dose aerosol generators, and measured the aerodynamic size of each particle real-time in the aerosol cloud by using the electronic single particle aerodynamic relaxation time (ESPART) analyzer. The ESPART works on the principle of Laser Doppler Velocimetry. Raw data was analyzed by adopting numerical methods. The normalized count median aerodynamic diameter and mass median aerodynamic diameter were found $2.99 \pm 0.08 \mu\text{m}$, and $3.93 \pm 0.09 \mu\text{m}$, respectively, which were comparable with the results reported by other investigators. Additionally it was found that the aerosol particles fraction per unit size distribution can accurately represent the aerodynamic size property. It is also concluded that scientists have taken a toxic chemical and made it useful to mankind over the time.

FRIDAY MORNING

Lakeview 2

Session 3

Chair: Dr. Ramaiyer Venkatraman

O3.13

9:00 DIELECTRIC PROPERTIES OF NOVEL FULLERENE-CONTAINING POLYURETHANE

Hanaa Ahmed, Steven Stevenson, Mohammad Hassan, Kenneth Mauritz, Paige Phillips
University of Southern Mississippi

C_{60} Fullerenol/polyurethane ($C_{60}(\text{OH})/\text{PU}$) and $\text{Sc}_3\text{N}@C_{80}$ fullerenols/polyurethane ($\text{Sc-MNF}(\text{OH})/\text{PU}$) nanocomposites were prepared from a simple reaction between diisocyanate end-capped prepolymer and different loadings of polyhydroxylated fullerenols in a solvent mixture of THF/DMF. The prepared nanocomposite films had high gel fractions ranging from 72-97% depending on the percent of the fullerenols added. Thermal Gravimetric Analysis (TGA) showed that the thermal degradation onset temperature of the prepared films increases with increasing gel fraction. The Dynamic Mechanical Analysis (DMA) showed loss peaks at approximately -60 °C corresponding to the glass transition temperatures, T_g , of the prepared films. The Dielectric properties of the prepared nanocomposites were studied over the frequency range 0.1Hz - 3MHz at fixed temperatures from -150 to 180 °C. The data obtained from dielectric spectroscopy showed that the dielectric constant, ϵ' , of fullerenol/PU nanocomposites increases with increasing fullerenol loading due to the

polarization contributions of the unreacted hydroxyl groups in $C_{60}(OH)$ or Sc-MNF(OH). Furthermore, ϵ' of Sc-MNF-PU is much higher than that of C_{60} -PU due to the presence of highly polarizable metals and induced dipoles inside the MNF cage.

O3.14

9:20 OLEFIN METATHESIS CATALYSTS BEARING PH-RESPONSIVE NHC LIGANDS

Shawna Balof, Hans Schanz

University of Southern Mississippi

We have synthesized several novel, ruthenium-based olefin metathesis catalysts bearing pH-responsive NHC ligands for external control of catalyst solubility based on ancillary NMe₂ groups. These catalysts perform ring opening metathesis polymerization (ROMP) of cyclooctene (COE) at faster rates than their commercially available counterparts and perform at similar rates during ring closing metathesis (RCM) of diethyl diallylmalonate (DEDAM) in organic media. These catalysts perform RCM of diallylmalonic acid in acidic protic media, however with only moderate activity, and do not produce polymer in the ROMP of a cationic 7-oxanorborene derivative. One catalyst was used for Ru-separation studies when RCM of DEDAM or 3,3-dialltpentadione (DAP) was conducted in low-polar organic solution. The Ru-species was subsequently precipitated by addition of strong acid and was removed by 1) filtration and 2) filtration and subsequent extraction with water. The residual Ru-levels could be reduced as low as 11 ppm without the use of chromatography or other scavenging methods. We are introducing a new synthetic strategy to develop a template synthesis that allows for the straightforward synthesis of several pH-responsive NHC ligand precursors and their corresponding catalysts.

O3.15

9:40 PERFORMNACE OF HYDRIDE GENERATION FOR SIMULTANEOUS DETERMIANTION OF BISMUTH, LEAD AND TIN BY ICP-AES IN BIOMINERALS

Domingos Afonso¹, Sitki Baytak², Zikri Arslan¹

¹*Jackson State University*, ²*Nevsehir University, Nevsehir, Turkey*

Heavy metals, such as arsenic, cadmium, lead, selenium and tin, are detrimental to ecosystem and human health at extremely small levels. Accurate determination necessitates the use of highly sensitive instrumentation and analytical chemistry methodologies. Inductively coupled emission atomic emission spectroscopy is a robust, multielement capable technique that takes the advantage of hot argon plasma to produce excited species. However, the sensitivity of ICP-AES is not adequate to detect these elements in environmental samples at low $\mu\text{g/g}$ levels due to the complexity of emission spectrum and inefficiency of solution nebulization. Hydride generation is popular

technique commonly used for flame atomic absorption spectroscopy for measurement of hydride forming elements. In this study, we examined the performance characteristics of hydride generation with ICP-AES for simultaneous determination of bismuth, lead and tin. The conditions were optimized for hydrochloric acid, potassium ferricyanide and sodium borohydride concentrations. To affect the hydride generation, acid concentration of the sample solutions were varied from 0 to 3% v/v. Solutions were mixed on-line with 3% $K_3Fe(CN)_6$ followed by reaction with 2% m/v $NaBH_4$ solution. The gaseous hydride was analyzed by ICP-AES. The detection limits varied between 0.10 $\mu\text{g/L}$ and 0.2 $\mu\text{g/L}$. The effects of various transition metals and hydride forming elements were investigated. Chromium, copper and nickel were found to suppress signals to some extent when present at high levels. The method was applied to the analysis of fish otoliths and bone ash samples.

O3.16

10:00 SYNTHESIS OF SEVERAL ANALOGUES OF UNNATURAL LYSINE FROM A COMMON SYNTHETIC INTERMEDIATE : FOR INCORPORATION IN SST14

Souvik Banerjee, Dale Jr Rossado, James W Wiggins, Douglas S Masterson

University of Southern Mississippi

Presently there has been extensive focus on the synthesis of unnatural alpha, beta and gamma Lysine, in order to incorporate them in the peptide specific cut sites of small peptides, such as Somatostatin. Because it has been already proven that incorporation of these unnatural amino acids increases the in vivo half life of these peptides and this is the important procurement for the cancer treatment. Our goal is to synthesize enantiomerically enriched Lysine analogues from a common synthetic intermediate and to incorporate them in the TRY-LYS cut site of the SST14 Peptide. The presence of the phthalimide protecting group in our Lysine chain helps us to obtain very high enantioselectivity in pig liver esterase hydrolysis of the prochiral diester Lysine derivative to get to the common half ester intermediate. Our synthetic route allows us to vary the chain length of the "R" group of the Lysine from 1 to n # of carbons, as well as to extend the carbon back bone from alpha to beta and from beta to gamma derivatives.

O3.17

10:20 THEORETICAL CALCULATION OF THE N-H STRETCH IN AMMONIA

Joseph Bentley, Ver Geshia Johnson

Delta State University

The potential energy curve for the N-H stretch in the ammonia (NH_3) molecule is modeled by fitting a data set generated by GAUSSIAN. The GAUSSIAN calculation was a restricted Hartree-Fock calculation with a 6-31G(d) basis set. The fitted potential energy curve was compared with the output from GAUSSIAN. Subsequently, the stretching vibrational wavenumbers were calculated using a one-dimensional model with a set of DVR points as a basis

set.

10:40 Break

Session 4

Chair: Dr. Karl J. Wallace

O3.18

10:50 DECIPHERING STRUCTURAL AND FUNCTIONAL FINGERPRINTS FOR PROTEINS

Yong Zhang, Yan Ling, Christopher Mills, Rebecca Weber
University of Southern Mississippi

Spectroscopic techniques are powerful tools to provide "fingerprint" information for biomolecular structures and functions. We use quantum chemical methods to accurately predict many spectroscopic properties and use such calculations with structural modeling and experimental spectroscopic data to determine protein structures. Recently, a critical reaction intermediate, oxyferryl species for tryptophan 2,3-dioxygenase (TDO) was reported, exhibiting a unique Mössbauer quadrupole splitting parameter that is noticeably greater than those of any other heme-based ferryl species but much smaller than those of protonated ferryl species. TDO is an important hepatic enzyme in the kynurenine metabolic pathway for energy production, neurotransmission regulation, and NAD biosynthesis. Our predictions of Mössbauer data have a theory-versus-experiment correlation coefficient $R^2=0.98$ and our computational investigations on possible structural influences from both the heme ligands and protein environment suggest that the unusual quadrupole splitting is a result of the hydrogen bonding to the oxo group in a unique active site environment, which for the first time discovered a role of hydrogen bonding to the critical oxyferryl species and was confirmed by recent mechanistic investigations. In another case, we enabled accurate predictions of three characteristic spectroscopic properties, ^1H and ^{15}N NMR chemical shifts and NO vibrational frequencies in synthetic HNO and RNO heme complexes, with $R^2 = 0.990-0.998$. Based on comparisons with experimental measurements for the first spectroscopically well characterized HNO-protein complex - MbHNO (Mb = myoglobin), a dual hydrogen bond mode for HNO in Mb was proposed for the first time, which can also account for its unusual stability observed experimentally.

O3.19

11:10 PHOTODEGRADATION OF NITROFLUORENES

Samuel Dasary, Jaunice Bronner, Amanda Fletcher, Ramaiyer Venkatraman, Hongtao Yu
Jackson State University

Nitro-PAHs are an important class of environmental pollutants. Polycyclic aromatic compounds are formed during incomplete combustion of organic material. In the presence of nitrogen oxides (NO_x), the neutral PAHs (such as fluorene) are converted into nitro-PAHs. NPAHs are also emitted from coal flyash, smelting,

effluent and engine exhaust. In the present work we have investigated. Photochemical degradation of 2-nitrofluorene (2-NF) and 2,7-dinitrofluorene (2,7-DNF). In a typical experiment 2-NF or 2,7-DNF in the concentration range of 50-100 μM were irradiated using 365nm wavelength UV light. UV-VIS absorbance change was used to monitor degradation. Further chromatographic techniques were used to identify the photoproducts. Our results showed that approx 60% degradation of the selected NPAHs was achieved following first order rate kinetics.

O3.20

11:30 EXTERNAL ACTIVITY CONTROL OF HEXACOORDINATE RU-ALLENYLIDENE AND INDENYLIDENE COMPLEXES

Samantha Pope, Hans J. Schanz
University of Southern Mississippi

Over the past four decades, metathesis has evolved to become a highly valuable and versatile tool in organic and polymer synthesis. Since the early 1990s ruthenium-based Grubbs-type Ru-benzylidene catalysts have immensely broadened the application spectrum of this reaction due to their high tolerance towards functional groups as well as moisture and molecular oxygen compared to homogeneous molybdenum-based systems. The technology today has evolved into a very important synthetic tool for the production of high performance materials as well as therapeutic agents.

A major drawback of the technology is the limited external activity control of the catalytic reactions. We have recently developed a reversible inhibition/activation protocol using basic N-donor ligands and non-nucleophilic acid which can function as an "off/on" switch for the reaction. Our research is focused on developing new systems with a variety of Ru-carbene complexes and N-donor ligands which allow for the external activity control based on this technology. We have synthesized and investigated Ru-carbene complexes for which the intellectual property is not protected (this has been a major obstacle in the commercial use of olefin metathesis thus far). We have investigated the effect of the external stimulus on the activity and stability of the catalytic Ru-species.

O3.21

11:50 TRANSFORMATION OF TRICLOSAN FACILITATED BY Fe(III)-SATURATED MONTMORILLONITE

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Triclosan (TCS) is a common antibacterial agent used in a wide array of pharmaceutical and personal care products. TCS is usually washed down to the sewer systems and ends up in the environment via wastewater effluent and biosolids. Once in surface water, a fraction of TCS can be transformed in to carcinogenic compounds such as 2, 8-dichlorodibenzo-p-dioxins. The main goal of this research

was to investigate the transformation of TCS in Fe (III)-saturated montmorillonite, a commonly found 2:1 aluminosilicate in soils. In this study, TCS was incubated in darkness with Fe (III)-saturated montmorillonite at different concentrations with and without the presence of water. The experiment was also conducted with the presence of HPLC grade water in darkness and under external fluorescent light source. The transformation products were characterized using HPLC/MS and quantified using HPLC/UV at different time intervals up to 100 days. Within 1 to 5 days, depending on the initial TCS concentrations, 50% of the TCS incubated with Fe (III)-saturated montmorillonite was rapidly polymerized into dimers and trimers. Similar transformation products, but in lower quantity were observed in the aqueous experiments with and without fluorescent light exposure. The dimer and trimer transformation products were stable over a period of 50 days and resistant towards further oxidation. SPARTAN-06 quantum mechanics program was used to evaluate the most possible structural confirmation of the dimer and trimer products. The calculations predicted two dominant dimers and trimers. The modeling results confirmed the experimental data obtained by HPLC/MS.

O3.22

12:10 AN INDICATOR DISPLACEMENT ASSAY FOR SENSING FE³⁺

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There has been plethora of new molecular sensors for the detection of heavy metals that utilize colorimetric or fluorescence mechanisms. An area of interest is the detection of total iron content (Fe²⁺ and Fe³⁺) in the ocean. There have been a number of large-scale "seeding" experiments carried out throughout the world to aid in CO₂ sequestration from the growth of algae blooms. We will report on the progress and development of molecular sensors, specifically to monitor Fe³⁺ in water, based on an Indicator Displacement Assay (IDA) that will utilize lanthanide ions as a sensing motif. Here we will discuss the synthesis of the molecular receptors, and our initial studies towards Fe³⁺ monitoring.

O3.23

12:30 ELECTROCHEMICAL AND ELECTROGENERATED CHEMILUMINESCENT STUDIES OF A RUTHENIUM(II) COMPLEX [Ru(pbt)₂(dpp)](PF₆)₂

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The electrochemical behavior of a ruthenium(II)-containing complex, [Ru(pbt)₂(dpp)](PF₆)₂ (where pbt = 2-(pyridine-2-yl) benzothiazole, dpp = 2,3-di(pyridine-2-yl) pyrazine] was studied in acetonitrile (MeCN) containing

0.10 M tetra-n-butyl ammonium perchlorate (TBAP). The complex displayed a reversible Ru^{II/III} redox process with E_{1/2} = +1.2 V vs Ag/Ag⁺ (10 mM), one reversible process of dpp/dpp⁻ with E_{1/2} = -1.26 V vs Ag/Ag⁺ and two reversible pbt/pbt⁻ couples with E_{1/2} = -1.45 V and -1.70 V vs Ag/Ag⁺ respectively at a Pt electrode, with a scan rate of 100 mV/s. Results of spectroscopic behavior, along with the electrogenerated chemiluminescence (ECL) of this complex obtained via ion annihilation and coreactant type ECL, will be presented.

12:50 Closing Remarks