ART CONSERVATION CHEMISTRY LABORATORY PROJECTS
(Joseph F. Lomax coordinator) Conservation Chemistry is a field of chemistry that deals with the challenges inherent in the preservation of art and artifacts. By its very nature it deals with time; it deals with items from the past in the present for the future. So in a sense, conservation chemistry is chemistry fully in four dimensions. Though impacted by all fields of chemistry, it is most allied to materials and analytical chemistry. Along with my collaborator, Dr. Suzanne Q. Lomax of the National Gallery of Art, I intend to write a book on Conservation Chemistry. It will be a 200-level general science course (prerequisite: general chemistry) with a lab component. The labs will include creation of artist materials such as paint, investigation into restoration techniques and use of one or more of a wide range of analytical techniques such as IR, Raman, NMR and X-Ray Fluorescence spectroscopies, as well as GC-MS and powder X-ray diffraction to examine composition and effects of time or various treatments on art materials. A number of specific projects are available; these could be pursued either for laboratory development or, in some cases, further research. This is where you come in. For each Capstone Project pair there will be three parts: 1) A familiarity with the techniques of conservation science will need to be obtained by reading selections provided from conservation manuals and the primary literature, 2) a literature search for currently available labs that can be adapted or used, 3) development and testing of a new lab experiment for inclusion into the course. The final product will have 2 – 3 tested labs and one new lab written up in a form that can be used in the text book. Proper literature acknowledgement will be given for all original work.

ATMOSPHERIC CHEMISTRY OF FORMIC ACID FORMATION
(Daniel W. O'Sullivan, coordinator) Aerosols are small particles suspended in the atmosphere and impact global climate, visibility and optical targeting. Early work recognized primary sources of aerosols directly emitted as pollution from industrial, automotive, and agricultural sources. Within the last decade a much more complex chemistry of aerosol formation has been recognized, and much work is occurring to understand the chemical processes which lead to secondary organic aerosol (SOA) formation. SOAs are not directly emitted from a source but form through gas phase or particle phase chemical reactions within droplets and constituents in ambient air. This project will examine the kinetics and controlling factors that influence the oxidation of methylhydroperoxide to formic acid in conditions found in atmospheric aerosol particles. The oxidation kinetics will be examined as a function of pH and temperature.

BIOPROSPECTING FOR NEW BIOFUELS AND NEW ANTIMICROBIAL COMPOUNDS
(Charles R. Sweet, coordinator) AIMS: Unexplored microbial populations represent a vast reservoir of potentially useful natural products. In this project, students will harvest, culture, and isolate bacteria from the air (prospecting the aeromicrobiome) or bacteria and algae from the Severn River (prospecting the estuarine microbiome). Successfully isolated and purified strains will be identified by microbiological and genetic means, and if they prove interesting will be incorporated into future USNA Chemistry research projects. SOW: This project will involve the preparation of microbial culture media, the isolation and propagation of microbial cultures, and the microbiological and chemical processes required to identify the cultures. This work will acquaint the students with the concepts and skills of organismal and molecular microbiology; it is strongly suggested that students have completed SB251 before undertaking this project. Note also that microbes do not adhere to academic schedules! While the expected effort in total is similar to other capstones, this project will require the flexibility to work varied hours, including the possibility of an occasional night or weekend.

CONSTRUCTION AND EVALUATION OF A SIMPLE SPECTROMETER
Many of the instruments we use in the instructional program are commercial instruments which, while very capable, do not give a real feel for the parameters being measured. This project involves the construction of a very simple spectrometer (colorimeter) using LEDs as light sources and a photocell (CdS or other device) as detector. Such a system is ideal for presenting the basic principles of spectrophotometric measurements, and it may find
later use in the IL or plebe chemistry sequence. A prototype has already been prepared as a demo for IL2, but much more work needs to be done to get quantitative results for real-world samples. This system is battery powered, and the detector circuity is very simple, so only a basic knowledge of EE is required! The initial system can be quickly constructed from PVC pipe and some LEDs to choose the wavelength, followed by evaluation of Beer’s Law with solutions absorbing in the visible region. Common applications can then be explored, such as iron or phosphate determinations. Another possibility is fluorescence measurements by monitoring the light beam at right angles to the LED beam. Comparison could then be made to the riboflavin determination you did in IL2 using a commercial instrument. A final possibility is a CCD-based spectrometer that would be useful for demonstrations of long-lived emitters, e.g. showing line spectra of discharge tubes. Trade-offs between the methods could be compared as well.

CONSTRUCTION AND CHARACTERIZATION OF A HOME-MADE DSC
The Differential Scanning Calorimeter (DSC) is an indispensable instrument for thermal analysis of complicated materials. While the commercial device, which you used in IL3 to explore phase behavior in mixtures, is quite sophisticated, the principles behind its operation are relatively simple – simple enough that you can build one yourself, for a fraction of the cost of the “real thing”. (See, for example, https://www.youtube.com/watch?v=DP0AMeft3vg). Aside from utilizing many skills you learned at the Academy (chemical, electrical, computer, etc.), and developing a deeper insight into the actual workings of such an instrument, the ability to create a useful low-cost instrument can extend techniques such as thermal analysis to educational institutions at all levels which otherwise could not afford them. This project involves construction of such a device and characterization of its behavior, including a comparison of performance with the much more expensive commercial system you used earlier.

CHEMISTRY RELATED TO FORENSIC INVESTIGATIONS
(Graham T Cheek, coordinator) The crime scene and forensic laboratory work highlighted in the CSI TV series stem from chemical and instrumental analysis fundamentals that you already have in your background. Surprisingly, in some cases there is only a practical, rather than first-principles, understanding of how the chemical characteristics of the evidence lead to the conclusions drawn from it. This project will involve attempting to make those fundamental connections. It could include a focus on (i) forensics of documents: characterizing common inks and paper by Raman spectroscopy and/or other techniques. The goal here is to find and tabulate unique features of ink and paper that could be used as markers for specific commercial inks, etc. Such information may make it possible to certify the nature of a document as genuine or forged. (ii) fingerprint development: How do fingerprint patterns get developed by reagents such as iodine, silver nitrate, SuperGlue, etc.? In many cases, the chemical reactions between the reagents and the components in fingerprint residue are not known. This project involves the reaction of specific reagents with typical fingerprint components such as amino acids, NaCl, fats and oils, etc. (iii) X-Ray Fluorescence and forensics: XRF provides non-destructive elemental analysis, particularly of metals, with micron resolution, and the capability to map composition of an evidentiary object. This feature can be applied to characterization of samples such as inks, toners, and small items recovered from a crime scene. Upon completion of this project, you will gain an appreciation of the types of techniques available to forensic investigators as they strive to bring justice to the criminal community.

“LAB-ON-A-CHIP”: STUDENT-FABRICATED MICROFLUIDIC DEVICES AS FLOW REACTORS IN SYNTHESIS AND/OR ANALYSIS
Microfluidic devices, also known as “labs-on-a-chip”, have gained tremendous popularity in many technological fields. These devices allow complex tasks such mixing, synthesis, sensing and separation to be carried out on miniaturized devices at the microliter scale. The reduced sample size, ease of controlling parameters, increased speed, and lower cost are highly attractive features of such systems. Current applications of the most sophisticated devices include biochemical and environmental monitoring, including sensing and identifying chemical warfare agents. In this project, midshipmen will design and create flow reactors on a microscope slide which permit the introduction, reaction, and sensing of products. Variations in the shape and size of flow channels can be used to explore the behavior of the reactors, and parallel studies of the reactions in the more familiar “batch” (vs. “flow”) mode will provide for a comparative study as well. A number of simple organic and inorganic reactions will be examined. Analytical applications may also be explored if time permits.
LABORATORY DEVELOPMENT PROJECT

The midshipmen will improve a current Integrated Laboratory (IL) or Plebe Chemistry experiment or develop a new IL or Plebe experiment that would be of interest to students. There are many candidates available for modifications of existing IL labs, such as incorporating ESR and XRF spectroscopy in IL4 labs; micelles in IL3, changing chemical systems in kinetics, spectroscopy or thermodynamics labs; etc. New labs could include luminescence quenching, etc. In the Plebe course, possible new labs or demos might be vapor pressure determinations for organic compounds, and exploring kinetic molecular theory approaches to the Bernoulli principle. Any new experiment must support concepts and techniques used in the IL or Plebe courses, and be feasible for use in a student laboratory. Instructor approval is required the first week of the semester.

HOW DO MICROWAVES HEAT A REACTION? Microwave Assisted Horner Emmons Reactions (Debra K. Dillner, coordinator) One of the newer areas of interest in synthetic chemistry is the use of specialized microwave ovens to accelerate reactions. Similar to home cooking applications, using microwaves for heating usually results in much shorter reaction (cooking) times and often to fewer by-products (burning). In conventional heating, the temperature increase in the reaction vessel is due to heating of the outside walls of the containers; this leads to heating of the interior contents indirectly, usually by warming the solvent and then having the solvent “heat up” the reactants, thus increasing the reaction rate. In contrast, most studies have indicated that microwaves heat the solvent directly. This implies that polar solvents, such as dichloromethane, should give better results than non-polar solvents. That sounds reasonable, but may not be true!

As part of a synthetic project, I attempted to use the microwave to accelerate a double-bond formation reaction, similar to a Wittig reaction. Successfully running the reaction in toluene, with standard heating, required temperatures over 100°C and reaction times over 72 hours - so any acceleration would be useful. Carrying out the same reaction in a microwave system gave some unexpected results. Using (nonpolar) toluene solvent and microwave heating to 150°C, the reaction was complete in about four hours. Using (polar) dichloromethane at 150°C, which should have accelerated the reaction even more, I found that the reaction took longer and gave lower yields! Why?

This project is to try to determine what factors are leading to this result, and whether these will be generally true for Wittig and Horner-Emmons reactions. One possibility is that in reactions like these, where one of the reactants is very polar, the maximum acceleration can be achieved by using non-polar solvents. The idea is that the reactant would absorb the microwaves and be heated directly, and the role of the solvent would be to “cool” the mixture. Carrying out the project would involve choosing a typical Horner-Emmons reaction, selecting a ketone and a suitable reagents. Then, you would carry out that one reaction under a variety of conditions, varying the solvent, the heating method and the reaction time. Once an optimum pairing of solvent/reagent is found, you could then investigate a variety of ketones or see if other reagents also follow the same pattern.

Usually, synthetic organic projects fulfill the Biochemistry option requirements since many of our targets are biologically active molecules and adding new methods for preparing them is important.

STUDENT DESIGNED PROJECT

In some cases it is possible to support midshipmen working on their own custom-designed chemistry projects. 

_Instructor approval is required the first week of the semester, or earlier!_