Research Activity: Separations and Analysis

Division: Chemical Sciences, Geosciences, and Biosciences
Primary Contact: William S. Millman (william.millman@science.doe.gov; 301-903-5805)
Team Leader: John C. Miller
Division Director: Eric Rohlfing (Acting)

Portfolio Description:

This activity addresses the scientific principles that underlie energy-relevant chemical separations and analytical methods, capitalizing on the relationships between these two areas of chemistry and Heavy Element Chemistry. It is focused around four main thrust areas along with a small assortment of other science themes. The thrust areas are:

- Laser based techniques: These rely on laser based spectroscopies and other techniques that provide the basis for analytical methods. Besides spectroscopy, lasers are used as probes or the initiator of a process that is ultimately quantified.
- Nanoscale science approaches to separations and analysis: These projects focus on aspects of the nanoscale that can be exploited to affect a separation or to understand the influence of the nanoscale on separations. These include nanoscale transport, synthesis of nanoscopic pores and structures, analysis of nanoscopic materials and relationship between nanoscale properties and chemical properties unique to the nanoscale.
- Ionization processes in analysis: This thrust is the major focus of mass spectrometry programs. It includes surface preparation and modification associated with mass analysis, and the interactions between ions and molecules and the transport and acceleration of ions in a vacuum and in the presence of various applied fields.
- Metal-adduct complexes for separations: This thrust is largely associated with extraction of trans-actinide elements. It includes the synthesis of ligands uniquely capable of interacting with specific elements. It also includes supramolecular complexes and other large structures such as micelles that can uniquely interact with transuranics along with their ability to attach or otherwise interact with surfaces and the resulting impact on selectivity.

The remaining activities are composed of a variety of projects such as those related to analysis of catalysts and catalytic phenomena, NMR analysis, droplet formation, solvation, a variety of synchrotron based analyses, and a growing new area in chemical imaging.

Unique Aspects:

This activity represents the nation's most significant long-term investment in solvent extraction, ion exchange, and mass spectrometry. The supported research is characterized by a unique emphasis on underlying chemical and physical principles, as opposed to the development of methods and processes for specific applications.

The portfolio for separations science emphasizes, but is not limited to, the separations of radionuclides and other metal ions, and seeks molecular-level understanding to support advances in both large-scale and analytical-scale separations. Molecular-level understanding is also sought for separations methods that have the potential to significantly impact energy use, such as membrane-based processes. Ionic liquids and supercritical fluid solvents are being explored with potential benefit to "green chemistry." The use and impact of nanoscale and supramolecular structures on various separations processes are of growing interest.

The analytical research portfolio has historically emphasized mass spectrometry and seeks to elucidate the chemical and physical principles that underlie ionization and excitation processes and modern approaches to mass discrimination. A more recent sector of the portfolio seeks to understand and use the interaction of electromagnetic radiation with matter in phenomena such as molecular fluorescence, laser ablation and surface-enhanced Raman scattering. Hyphenated laser-mass spectrometry techniques such as MALDI-MS, laser ablation ICP-MS, and laser ionization ion mobility-MS are being explored. The extension of these ultrasensitive techniques to single-molecule detection and observation is being explored. Research to understand chromatography at the molecular level reflects the synergy between separations and analytical sciences. This activity also contributes to the maintenance of the scientific infrastructure required to meet as-yet-undefined challenges in separations and analysis.

Relationship to Other Programs:

The activity is closely coupled to the Department of Energy (DOE) stewardship responsibility for actinide and fission product chemistry and to its clean-up mission. The activity emphasizes the separations and analysis of actinide and fission product elements and their decay products. Some overlap and coordination with the BES Heavy Element Chemistry Program is natural. Similarly, elements of the analysis science portfolio benefit from cooperation with the BES Catalysis and Chemical Transformations, Chemical Physics, Materials Chemistry, and Atomic and Molecular Science Programs. The basic nature of the research has led to advances in technologies ranging from those that support nuclear non-proliferation efforts, to efforts in the President's Hydrogen Fuel Initiative, and to aspects of the Human Genome Project.

Significant Accomplishments:

This activity is responsible for such notable contributions as the concept of host-guest complexation, for which Professor Donald Cram (University of California, Los Angeles) shared the 1987 Nobel Prize in Chemistry; the use of the inductively coupled plasma (ICP) for emission and mass spectrometry; the development of the TRUEX process based on the ligand design work of Dr. Phillip Horowitz; Dave Dahl's development of SIMION, a program to simulate the motion of ions in fields that has become the standard tool internationally for development of ion lens; and, more recently, the development of BOB, a calixerene ligand that complexes Cs+ which is based on design and development work of Bruce Moyer at Oak Ridge National Laboratory (ORNL) and is being used to clean up waste tanks at Savannah River National Laboratory (SRNL).

Mission Relevance:

The success of the Manhattan Project was, in large part, due to our ability to develop industrial-scale processes for separating plutonium from irradiated fuel. Thus began the intense interest of DOE and its predecessor agencies in the science that underlies separations processes. The missions of DOE have evolved, and it must now face the legacy of accumulated wastes from the cold war era. Knowledge of molecular-level processes is required to characterize and treat these extremely complex mixtures and to understand and predict the fate of associated contaminants in the environment. In addition, separations science and technology have huge economic and energy impacts. For example, distillation processes in the petroleum, chemical, and natural gas industries annually consume the equivalent of 315 million barrels of oil (~5.4% of total petroleum consumption). It is further estimated that separations processes account for more than 5% of total national energy consumption. Separations are essential to nearly all operations in the processing industries and are necessary for many analytical procedures.

Likewise, DOE and its predecessors were also driven to develop analytical methodologies to support their early missions. Nuclear and radiochemical analyses were supported and refined by developments in analytical separations, such as solvent extraction and ion exchange. A need for reliable potentiometric titration prompted the first use of operational amplifiers in analytical chemistry and led to a revolution in electrochemistry. Mass separations was required for assay in the form of mass spectrometry and, in the form of the calutron, served as the first method for the production of macroscopic quantities of separated isotopes of uranium and other elements. As with separations science, improved understanding of the underlying science is required to meet the analytical challenges presented by the legacy of the Cold War and the future challenges of DOE as its missions and responsibilities continue to evolve.

Scientific Challenges:

Challenges in separations science include the development of a deeper understanding of processes driven by small energy differences. These include self-assembly and molecular recognition, crystallization, dispersion, coalescence, and hysteresis in transport properties of glassy polymer membranes. The development of fundamental principles to guide ligand design for atomic and isotopic specific recognition and separations is also required. These, in turn, pose challenges to analysts to generate the understanding required to characterize amorphous materials through analysis of scattering data or other methods. Other analytical challenges include single-molecule detection and direct observation of bimolecular interactions and reactions. A deeper understanding of laser-material interactions as well as ionization and excitation sources for optical and mass spectrometric analyses is also required. Significant challenges are posed by elucidation of principles to underlie diagnostics at interfaces between synthetic materials and biomolecules, at oxide-aqueous interfaces, and to monitor spatial and temporal processes in, and on the surfaces of living cells. Though understanding at the molecular level is required, there is currently insufficient knowledge to extend that understanding from the molecular level to the nanoscale, to mesoscale, and finally, to macroscale phenomena. Pursuit of that knowledge presents a major challenge to this activity.

Funding Summary:

Dollars in Thousands

FY 2005	FY 2006	FY 2007 Request
15,490	17,287	24,041

Performer	Funding Percentage (2005)
DOE Laboratories	56%
Universities	44%

These are percentages of the operating research expenditures in this area; they do not contain laboratory capital equipment, infrastructure, or other non-operating components.

This activity provides funding for about 50 university grants supporting, at any given time, on the order of 60-70 graduate students and 25-30 postdoctoral associates. In addition, 14 programs at DOE national laboratories support numerous senior staff, and additional students and postdoctoral associates. Programs at the national laboratories are typically multi-investigator efforts on problems that require extensive collaboration by senior scientists and postdoctoral associates. These programs act as the focal point for specific research efforts vital to the DOE mission. This activity supports research programs at ORNL, Argonne National Laboratory (ANL), and Pacific Northwest National Laboratory (PNNL), with smaller efforts at Ames Laboratory, and Lawrence Berkeley National Laboratory (LBNL). Many of the research efforts at the national laboratories involve collaborations with the university and industrial communities.

Projected Evolution:

Separations research will continue to advance the understanding of multifunction separations media; supramolecular recognition (using designed, multi-molecule assemblies to attract specific target species); synthesis of new porous materials and control of interface properties at the nanoscale; ligand design and synthesis of extractant molecules; mechanisms of transport and fouling in polymer and inorganic membranes; solvation in supercritical fluids; field-enhanced mixing; and drop formation.

Analytical research will pursue the elucidation of ionization and excitation mechanisms for optical and mass spectrometry; single molecule detection, characterization, and observation; nano- and molecular-scale analytical methods; laser-based methods for high-resolution spectroscopy and for presentation of samples for mass spectrometry; characterization of interfacial phenomena, with emphasis on chromatography; surface-enhanced Raman spectroscopy; and use of quadrupole ion traps to study gas-phase ion chemistry.

An expanded activity would support work to understand the underlying science needed to image molecular assemblies and molecules in space and time to enable new advances in science. The program is now in a position to begin doing experiments similar to those in microscopy that brought about a revolution our understanding of cells as the underlying structure that supports life.