Research Activity: **Separations and Analysis**
Division: Chemical Sciences, Geosciences, and Biosciences
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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 with Heavy Element Chemistry. The portfolio focused around five main thrust areas: 1) Laser-based techniques, including laser spectroscopy and other quantitative analytical techniques; 2) Nanoscale science approaches to separations and analysis, including transport, synthesis of nanoscale pores and structures for separations, analysis of nanoscale materials, and chemical properties unique to nanoscale materials; 3) Ionization processes in analysis, particularly mass spectrometry, including surface preparation and modification, the interactions of ions and molecules, and the transport and acceleration of ions in the presence of applied fields; 4) Metal-adduct complexes for separations, particularly trans-actinide elements, including synthesis of ligands uniquely capable of interacting with specific elements, supramolecular complexes, micelles, and proteins that display unique separation selectivity; 5) Advancing molecular-scale or chemical imaging, including pushing frontiers in spatial and temporal resolution.

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.

Relationship to Others:

The activity is closely coupled to the Department's stewardship responsibility for actinide and fission product chemistry and to its clean-up mission. It emphasizes the separation 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 Science, Chemical Physics, Materials Chemistry, and Atomic, Molecular, and Optical 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 the Advanced Nuclear Energy Initiative.

Major Accomplishments:

This activity is responsible for such notable contributions as the concept of host-guest complexation, for which Professor Donald Cram (UCLA) 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 the Department of Energy and its predecessor agencies in the science that underlies separation processes. The missions of the Department have evolved, and it must now face the legacy of accumulated wastes from the cold war era and the growing emphasis on alternative energy sources. Knowledge of molecular-level processes is required to characterize and treat the extremely complex mixtures associated with cleanup and to predict the fate of associated contaminants in the environment. In addition, separation 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% of total petroleum consumption). Overall, it is estimated that separations processes account for more than 5% of total national energy consumption. This need is increasingly apparent with incipient technologies for alternative energy sources. Separations are essential to nearly all operations in the processing industries and are necessary for many analytical procedures.

Likewise, the Department 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 separation 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 separation science, improved understanding of the underlying science is required to meet the analytical challenges presented by the legacy of the cold war, alternative energy sources, and the future challenges of the Department as its missions and responsibilities continue to evolve.

Scientific Challenges:

Challenges in separation 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 2007	FY 2008	FY 2009 Request
15,860	15,860	28,338

Performer	Funding Percentage (2007)
DOE Laboratories	54%
Universities	46%

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 students and 25-30 postdocs. In addition, 14 programs at national laboratories support numerous senior staff, and additional students and postdocs. Programs at the laboratories are typically multi-investigator efforts on problems that require extensive collaboration by experienced scientists. These programs act as the focal point for specific research efforts vital to the DOE mission. This BES 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 achieve true chemical imaging, i.e., the ability to selectively image selected chemical moieties at the molecular scale and to do so with temporal resolution that allows one to follow physical and chemical processes.