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 synergistic relationship between these two areas of chemistry.

The portfolio for separations science emphasizes, but is not limited to, the separation 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 separation methods that have the potential to significantly impact energy use, such as membrane-based processes.

The analytical research portfolio emphasizes mass spectrometry and seeks to elucidate the chemical and physical principles that underlie ionization and excitation processes and modern approaches to mass discrimination. A second major sector of the portfolio seeks to understand and use the interaction of electromagnetic radiation with matter in phenomena such as molecular fluorescence, laser ablation, surface-enhanced Raman scattering, and magnetic resonance. 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.

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. The basic nature of the research has led to advances in technologies ranging from those that support nuclear non-proliferation efforts to 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 (UCLA) shared the 1987 Nobel Prize in Chemistry; the use of the inductively coupled plasma (ICP) for emission and mass spectrometry; and, more recently, the concept of bifunctionality in ion-exchange resins and solvent extraction. A Presidential Green Chemistry Award in 1997 was shared by researchers supported by this activity for their contributions to the understanding of processes in supercritical carbon dioxide that enabled the introduction of a chloro-fluorocarbon-free process for the dry-cleaning industry. This new commercial process relies on fundamental understanding developed with the support of this activity.

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. 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, 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 (~5.4% 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.

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 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. Improved understanding of solvation in supercritical and other fluids is required, as is the development of fundamental principles to guide ligand design. 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 2000	FY 2001	FY 2002
$12,255	$14,393	$13,047

Performer	Funding Percentage
DOE Laboratories	53.0%
Universities	47.0%

This activity provides funding for 47 university grants supporting about 57 students, 29 postdocs, and partially supporting about 44 faculty and senior staff and 22 programs at national laboratories supporting numerous senior staff, and additional students and postdocs. Programs at the laboratories are typically multi-investigator efforts on problems that require extensive participation by experienced scientists. These programs act as the focal point for specific research efforts vital to the DOE mission. This BES activity supports research at ORNL, ANL, and PNNL, with smaller efforts at LBNL, BNL, and INEEL. 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; self-assembly for supramolecular recognition (using designed, multi-molecule assemblies to attract specific target species); synthesis of ionophores (molecules that attract charged species); molecular-level understanding 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 characterization of interfacial phenomena, with emphasis on chromatography; second-order phenomena in NMR spectroscopy; elucidation of ionization and excitation mechanisms for optical and mass spectrometry; single molecule detection and characterization; nano- and micro-scale analytical methods; laser-based methods for high-resolution spectroscopy and for presentation of samples for mass spectrometry. Enhanced Raman spectroscopy will be investigated and exploited. The use of quadrupole ion traps to study gas-phase ion chemistry will continue.

An expanded activity would support work to understand the self-assembly process by investigating energetics and rate-controlling steps; increased effort in characterization of the aqueous-oxide interface, as well as general liquid-solid and liquid-liquid interfaces; analysis of scattering and NMR data to characterize amorphous media; extension of solid-state NMR to more elements in the periodic table; enhanced effort in molecular modeling to support ligand design; improved analysis of near-edge x-ray absorption to directly probe electronic states ultimately responsible for chemical reactions; field-enhanced spectroscopy; expand university effort in manpower-intensive organic and inorganic synthesis; provide support to enhance collaboration between universities and national laboratories; and maintenance and upgrade of national laboratory infrastructure. The activity will evolve to meet the challenges in self-assembly, characterization of interfaces, single-molecule detection, and gas-phase ion chemistry. A synthesis of results of analytical research to enable collection of basic data, ligand design to control possible reactions, as well as modeling and computational science, will be required to enable the prediction of macroscopic behavior from known molecular properties.

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