NISTIR 5828

Chemical Science and Technology Laboratory

CSTL Technical Activities 1995

U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Institute of Standards and Technology
Submitted to the Board on Assessment of NIST Programs, National Research Council

Shown on the cover (clockwise starting at the top):

A secondary ion mass spectrometry image of a pattern formed by using photolithography to "write" mercaptoundecanoic acid molecules into a monolayer of perfluorinated alkylthiol molcules. Microarrays of molecules such as these may be useful components of miniaturized biosensors and diagnostics devices of the future.

Standard Reference Materials (SRMs) for the qualitative and quantitative analysis of oxygenates in gasoline. NIST is working with the American Industry/Government Emissions Research (AIGER) consortium to assist the automotive industry in accurately measuring exhaust components.

An early time point in a simulation of the collision of two 120 atom silicon clusters based on atomistic calculations. The calculations are used to obtain physical, thermochemical and kinetic properties relevant to nanoparticle growth.

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Submitted to the Panel for the
Chemical Science and Technology Laboratory
Board on Assessment of NIST Programs
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Hratch G. Semerjian, Director
Chemical Science and Technology Laboratory
National Institute of Standards and Technology

U.S. DEPARTMENT OF COMMERCE, Ronald H. Brown, Secretary
Technology Administration, Mary L. Good, Under Secretary for Technology
National Institute of Standards and Technology, Arati Prabhakar, Director

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Chemical Science and Technology Laboratory

Hratch G. Semerjian, Director
William F. Koch, Deputy Director

Program Overview

The National Institute of Standards and Technology's unique mission is to promote U.S. economic growth by working with industry to develop and apply technology, measurements, and standards. In response to this challenge, we have expanded our interactions with U.S. industry to meet their needs and help improve their global competitiveness, while continuing to provide the national system of chemical and physical measurements, the fundamental research base for tomorrow's chemical science and technology, and a national reference laboratory to address critical problems related to public health and safety. Our ***vision*** is to be a world class research laboratory recognized by the Nation as the primary resource for measurements, data, models, and reference standards in chemistry, biotechnology, and chemical engineering required to enhance U.S. industrial competitiveness in the world market.

Mission:
As the Nation's Reference Laboratory, the ***mission*** of the Chemical Science and Technology Laboratory is to perform research in measurement science; develop and maintain measurement methods, standards, and reference data; and develop models for chemical, biomolecular and physical properties and processes. CSTL provides the enabling infrastructure to enhance productivity and competitiveness; assure equity in trade; and improve public health, safety and environmental quality for the U.S. industry, government agencies, and the scientific community.

The ***goals*** of CSTL are to (1) establish CSTL as the pinnacle of the traceability structure for measurements in chemistry, chemical engineering, and biotechnology; (2) assure that U.S. industry has access to accurate and reliable data, models, and predictive algorithms; (3) anticipate and address next generation measurement needs of the Nation; and (4) foster the discovery and development of advanced process technologies.

As part of the ongoing strategic planning process within CSTL and to respond to national challenges, opportunities, and the needs of our customers, we have focused our programs in five thrusts of strategic importance: biotechnology, process technology, environmental technologies, health care technology, and fundamental measurement technology. These **strategic thrusts** link the four goals to specific program directions and technical activities.

Our current activities address important areas within the mission of CSTL. We use many avenues to successfully accomplish our mission and goals including: providing Standard Reference Materials (SRMs), calibrations and Standard Reference Databases (SRDs), research with industry through Cooperative Research and Development Agreements (CRADAs) and sponsorship of consortia, licensing patents, research publications and talks, and measurement services. Accomplishments in FY95 are summarized in the table below.

Organizational Structure:
In order to achieve the laboratory's technical goals, CSTL maintains a highly trained technical staff. The permanent staff numbered 278 in FY95 with an additional 84 temporary and part-time employees. Also, there were nearly as many guest scientists (260) as permanent staff. The technical staff consisted of 122 chemists, 44 physicists, 34 engineers, and 15 biologists. A staff of 29 provided technical support.

Div	Pubs.	Talks	Committees[1]	Seminars	Conferences	CRADAs	Patents	SRMs	SRDs	Cals.[2]
830	1	8	18	11	1	0	0	0	0	0
831	104	86	58	28	10	12	5	1	1	0
833	93	47	41	22	4	2	0	0	2	0
836	72	75	81	19	5	14	2	3	1	729
837	90	109	54	11	8	6	0	5	4	8
838	125	89	86	30	3	5	1	0	6	108
839	144	158	122	10	9	22	1[3]	165	0	325
Totals	629	572	460	131	40	61	9	174	14	1170

[1]Committee totals include 65 editorships
[2]Calibrations were performed for over 500 customers
[3]Joint with 831

Division Key:

830	Laboratory Office
831	Biotechnology Division
833	Chemical Kinetics and Thermodynamics Division
836	Process Measurements Division
837	Surface and Microanalysis Science Division
838	Thermophysics Division
839	Analytical Chemistry Division

Some important changes were made in the CSTL management structure in FY95. At the beginning of FY95, the Inorganic (834) and Organic (835) Analytical Research Divisions were combined, under the leadership of Willie May, to form the Analytical Chemistry Division (839). Former 834 *Chief*, William Koch became *CSTL Deputy Director*. Walter Stevens became *Chief* of the Biotechnology Division when Lura Powell left CSTL to become *ATP Director*, mid-year. The *Chief* of the Chemical Kinetics and Thermodynamics Division, Sharon Lias, retired recently.

We strive to achieve a balance between providing essential measurements and technology, and carrying out basic research to ensure a healthy science and infrastructural technology base for the future. Each Division in CSTL performs basic and applied research, and maintains close contacts with the appropriate industrial and scientific communities.

Technical Achievements:

There were many noteworthy technical achievements by CSTL scientists and engineers during FY95, examples of which are presented below. More detailed information about these activities can be found in the appropriate Division's selected technical highlights.

In FY95, CSTL staff produced a number of outstanding ***research accomplishments*** serving a great diversity of constituents. The Biotechnology Division released a new standard reference material, **SRM 2391**, which is a **Polymerase Chain Reaction-based DNA profiling standard** developed for the forensic and paternity testing communities (831). We designed and began the initial characterization of a **DNA Sequencing Standard, SRM 2392**, which is needed for quality assurance in the growing commercial applications of DNA sequencing in disease diagnosis.

The Process Measurements and Thermophysics Divisions initiated a competence project, joint with the Radiometric Physics Division of the Physics Laboratory, to improve the accuracy of **thermodynamic temperature measurements** in the range above 500 K (836 and 838). A major new **calibration and testing facility for gas flowmeters for vehicle exhausts** was constructed as part of our collaboration with the American Industry/Government Emissions Research (AIGER) consortium (836 and 839).

A major thrust in the semiconductor area is to address industry's needs for reliable and accurate flow measurements in the important range from 0.1 to 100 cm^3/min (10^{-7} to 10^{-4} mol/s). During the past year, researchers in the Thermophysics Division have constructed two new **constant-volume primary flow standards** based on the pressure rate-of-rise technique and have shown that they agree with existing constant-pressure primary flow standards to within 0.1% (838). In addition, they have developed a very robust **transfer standard for low flows** based on a laminar-flow element of novel design. This device will enable NIST to transfer the required flow measurement accuracy to industrial laboratories (838). To improve primary pressure standards, CSTL has initiated a collaboration with an industrial partner, DH Instruments, Inc., to characterize the **world's first 50-mm-diameter piston gages**; these large-diameter gages have the potential to become primary standards in the important range near atmospheric pressure. Efforts were completed to provide a **new service for calibrating gas-operated piston gages up to 110 MPa**, extending our capabilities for gases above our previous limit of 16 MPa, to a pressure range of importance in many industrial applications (838).

As part of our effort to advance microparticle characterization technology, the Surface and Microanalysis Science Division developed an **automated probe measurement and presentation technique** for the simultaneous visualization of spectral and isotopic data from thousands of individual particles (837).

The Analytical Chemistry Division made a significant advance in the **separation technology** available for the analysis of nutritionally important carotene compounds. By designing and characterizing custom liquid chromatographic separation columns, all of the major isomeric polar and non-polar carotenoids can be separated and identified. The improved measurements will help medical researchers evaluate the benefits of a diet high in carotenes on the incidence and recurrence of cancer. This new column technology has been transferred to industry and is widely available from YMC, Inc (839).

Measurement Services:

In FY95, we devised a plan to improve our **NIST Traceable Reference Material** (NTRM) program, established in FY93 to provide our customers with a more readily available alternative to gas SRMs. For production of a NTRM, a specialty gas producer manufactures a batch of gas mixtures of specified composition and quality, makes measurements on each mixture, and provides all of the data and a selected subset of the batch to NIST for quality assurance measurements, statistical analysis and value assignment. The producer can than sell them to customers, use the NTRM batch to produce other NIST traceable gases, or produce EPA protocol gas standards. Starting in FY96, we will expand the availability of NTRM gas mixtures to include any composition for which we have primary standards (839).

CSTL also provides the powerful **Mass Spectral Database** for the identification of chemicals of medical, environmental, and industrial importance. In FY95, Microsoft Windows™ Version 1.5 of this popular Standard Reference Database was released. It provides such powerful and user-friendly identification, automation, and library search tools that two thirds of all mass spectrometer instruments sold in the U.S. include this database. The large compound library (62,000+ entries) is currently being expanded to include all commercially available chemical compounds.

To meets its goals of improved measurements in the field, the American Petroleum Institute (API) has requested CSTL to reduce its quoted uncertainty for the calibration of volume test measures by a factor of four, down to 0.01%. As a result, CSTL, in a cost-shared project with API, is constructing **a new primary standard facility for liquid volume measurements**. The approach used is to determine volumes by weighing the distilled water required to fill a volumetric test measure to the reference mark, measuring the water temperature, and calculating the volume from the density equation for water (836).

Publications and Talks:

A significant new approach to **modeling the solidification of fluids** quenched below the thermodynamic triple point was developed and

published in the journal *Physical Review Letters*. The model, which utilizes molecular dynamics simulation methods and which is based on a fractal analysis of the evolving structures, accurately describes the system during the change from a fluid to the solid state. An analogy to an important process - the formation of a gel - is drawn (838).

A series of reviews on the **thermodynamics of enzyme-catalyzed reactions** has been completed by scientists in the Biotechnology Division. The reviews contain evaluated data for the six major classes of enzymes: oxidoreductases, transferases, hydrolases, lyases, isomerases, and ligases. These data, which are useful in the optimization of industrial bioprocesses, will be made available on the World Wide Web in 1996 (831).

This year we completed development and publication of an extensive **chemical kinetic mechanism for high temperature fluorocarbon chemistry** in the journal *Progress in Energy and Combustion Science,* which will find application in the areas of plasma etching and polymer formation, as well as in fire suppression, incineration, and atmospheric chemistry. The development of this mechanism relies heavily on the use of **computational chemistry**, a tool which is of great value for quantitative estimation of important reaction intermediates and rates throughout our materials chemistry and semiconductor models and data programs (836).

A new **International Position on Detection and Quantification Limits in Chemical Metrology**, that promises to have a metrological impact analogous to that of uncertainty, was documented with the publication of the official recommendations of the International Union of Pure and Applied Chemistry. This document establishes the conceptual and practical basis for chemists to evaluate these fundamental performance characteristics and to adopt a common nomenclature and approach to detection decision-making. The influence of this work extends to coordinated efforts with **ISO**, and to requests for guidance from ASTM and US EPA. The new international position was presented in an invited talk to regulators, academic scientists, chemists and statisticians at the **International Conference on Environmetrics and Chemometrics** in September 1995 (837).

A critical review of **contamination associated with ion implantation** to modify or produce electronic devices such as semiconductors, and the characterization of the contamination by secondary ion mass spectrometry (SIMS) was published in the journal *Solid State Technology*, in collaboration with four industry authors. The organization of the publication is unusual as it follows the path of the ion beam through an ion implanter, beginning with the ion source and continuing to the end station. At each stage, origins of contamination are explained and the unique ability of SIMS to detect and identify specific contaminants is demonstrated (837).

"Standardless" analysis is widely employed practitioners of electron microprobe measurements because of its apparent simplicity and its inclusion with software supplied with the instruments. Using **NIST-NIH Desktop Spectrum Analyzer (DTSA)**, a comprehensive software engine for electron-excited X-ray spectrometry, we have shown that a severe loss in analytical accuracy occurs when "first principles 'standardless'" analysis is employed, compared to the accuracy achievable with the more rigorous approach of measuring standards and calculating matrix corrections. This joint NIST-NIH work, published in the journal *Analytical Chemistry*, is critical to re-establishing the **credibility of quantitative electron probe X-ray microanalysis** in the analytical community, which has been significantly eroded because of reported inaccuracies (837).

CRADAs, Consortia, and ATP Collaborations:
After five years, the **Consortium on Automated Analytical Laboratory Systems (CAALS)**, with its 20 industrial and two government members, is bringing its work on standards for laboratory automation to completion. Products of the CAALS effort are coming out in the form of NIST Internal Reports and external publications. A draft ASTM standard on laboratory equipment control interface specifications is being prepared by working group E49.52 and is based primarily on CAALS work (839).

A decision has been made to **disband the Consortium for Advanced Biosensors (CAB)** in the Spring of 1996. For the last two years, CAB research has focussed on the measurement and control of non-specific binding of proteins to surfaces. This phenomenon diminishes the specificity and sensitivity of biosensing devices, and represents a serious impediment to biosensor development. CSTL scientists carried out a series of experiments, using self-assembling surface monolayers, to quantify the non-specific binding of representative proteins to surfaces with known chemical and physical characteristics. Unfortunately, recent corporate reorganizations and down-sizings have made it difficult to maintain the CAB membership above a critical level (831).

As part of a CRADA with several industrial partners, the Fluid Flow Group in the Process Measurements Division has initiated an **Air Speed Proficiency Testing Program** to quantify the performance of anemometer calibration facilities operated by anemometer manufacturers, calibration laboratories, and users. A round-robin testing process will be designed and used to produce practical data indicative of calibrator performance. The results will provide an assessment of accuracy and a basis for claiming realistic air speed measurement traceability to NIST for the participants (836).

In our CRADA with X-Ray Optical systems, we have identified defects in **developmental x-ray focusing optics** using a newly constructed x-ray test bench, providing invaluable measurements that are critical to improving commercial production (837).

CSTL also performed measurement research in technical areas identified by ATP awards. Twenty four internal research projects were selected for ATP sponsorship in areas defined both by the general and focussed competitions. CSTL researchers made a particularly significant contribution to the focussed program in "Tools for DNA Diagnostics" with projects in DNA standards, in chemistries for sequence-specific recognition to support DNA-on-a-chip technologies, and in sensor development.

In addition, CSTL staff contributed to the road mapping activities that lead to development of new ATP focussed programs, including those in the areas of catalysis/biocatalysis and separations. Several CSTL staff members also made significant contributions to the technical assessment process for selection of ATP awardees.

Patents:

In FY95, 8 patents were awarded to CSTL researchers. A third patent on the **micro-hotplate gas sensors** was received and more that 25 companies have shown interest in licensing this technology (836).

Several biotechnology-related patents were awarded in FY95. A method for **liposome immunoanalysis by flow injection assay** deals with the use of liposomes as carriers of detectable reagents in a flow injection system (831 and 839). **Matrix modification in the electrophoretic separation of nucleic acids** deals with the enhancement of the separation of polynucleotides or polypeptides of various chain lengths by modifying the matrix of an electrophoretic gel (831). Among the several new patent applications filed in FY95 was a new electrochromatography method, which allows for the **rapid separation and purification of DNA** from mixtures of DNA and other materials including proteins (831).

Conferences and Workshop:

CSTL was the host of the **50th Calorimetry Conference** in July of 1995. Two Hundred and Thirty Eight presentations were made covering thermodynamic measurements of compounds important to the chemical industry, biology and biotechnology, and the nuclear power industry. In March of 1995, a **workshop on "Treatment of Gaseous Emissions via Plasma Technology"** focused on the use of plasma process technology to reduce atmospheric emissions. The workshop was co-sponsored by CSTL, Batelle Pacific Northwest Laboratory, and the Strategic Environmental Research and Development Program and had 120 scientific and engineering attendees. A workshop report is available. A **"Telepresence Microscopy Working Group" meeting** was held at NIST in January, 1995. This group is a collaboration of Argonne, Sandia, and Oak Ridge National

Laboratories, NIST and Lehigh University and seeks to promote the remote operation of microscope instrumentation. CSTL staff also organized 2 major conferences off-site, the **"Sixth Topical Conference on Quantitative Surface Analysis"** in Minneapolis (October 1994) and the meeting of the International Standards Organization's **"Technical Committee 201 on Surface Chemical Analysis"** in Golden, CO (October 1994).

External Activities:
CSTL staff participated in many external activities to assist industrial, standards, or other government organizations. Willie May was appointed Rapporteur of the **Chemical Metrology Subcommittee of NORAMET**, the collaborative body establishing standards intercomparability in the Americas. Hratch Semerjian and Robert Watters are the NIST representatives to the **Consultative Committee on the Quantity of Material for the CIPM**, harmonizing standards with European countries.

Scientists in the Biotechnology Division have converted the **NIST/NASA/CARB Biological Macromolecule Crystallization Database** (BMCD) into one of the first NIST Standard Reference Databases to be made available in fully interactive form on the World Wide Web. The database, which contains several thousand entries, is used to develop biomacromolecular crystallization protocols by analyzing published data on previously successful crystallization experiments. The BMCD was expanded recently to include data from microgravity experiments conducted by NASA onboard the space shuttles.

The combination of an expanding global marketplace and the required compliance with Quality Guidelines such as the International Standards Organization's ISO 9000 as a criteria for trade, is making new demands on the accuracy and traceability of chemical and physical measurements and standards. To meet this demand, CSTL expanded its efforts to assure the comparability of standards between nations. We have helped to establish a **Quality Assurance Program for Aquatic and Atmospheric Environmental Chemical Measurements** within our regional standards group, NORAMET, established by the 3 current NAFTA countries, the U.S., Canada and Mexico. To assure acceptance of NIST standards and measurements, we have established a timetable for round robin measurement comparison exercises for selected materials. We have also established a guest researcher program with Mexico's standards organization, CENAM, to help share our measurement expertise and establish collaborative projects (839).

CSTL and the National Measurement Institute of the Netherlands have signed a memorandum of understanding for an **intercomparison study of primary gas standards mixtures.** The measurement criteria for a "Declaration of Equivalence" of each nation's standards has been defined and a timetable for evaluation of selected gas mixtures has been established (839).

CSTL and the national standards laboratory for Germany (PTB) have completed the first international intercomparison of **ultra-high vacuum standards**. Using two ionization gage transfer standards (Bayard-Alpert and extractor ionization gages) the measured differences between the standards of the two laboratories were found to be well within their combined uncertainties (838).

In FY95, CSTL participated in an **international comparison of humidity standards**, coordinated by Spain's INTA Laboratory. A transfer standard hygrometer from the European Union region was calibrated against a NIST calibration standard. The agreement between CSTL results and those previously obtained on the transfer standard by the U.K.'s NPL was excellent.

In our continuing effort to support the **realization of the International Temperature Scale of 1990** (ITS-90), we performed intercomparisons of triple-point water temperature cells between NIST, CENAM (Mexico), NIM (China) and UME (Turkey).

In order to provide our customers with rapid access to CSTL information, CSTL established a **"home page" on the World Wide Web** near the end of FY95. The URL is **http://www.cstl.nist.gov**.

Awards and Recognition:
Many CSTL scientists received awards and recognition. Charles Beck won the 1995 **John L. Hague Award**, presented by ASTM Committee E-1 on Analytical Chemistry for Metal-Bearing Ores and Related Materials. Heather Chen and David Mildner received the **R&D 100 Award** for the development of the Glass Polycapillary Neutron Focusing Optic with collaborators form X-ray Optical Systems and SUNY Albany. Hratch Semerjian received the Department of Commerce **Gold Medal** "for managerial and scientific leadership as director of the Chemical Science and Technology Laboratory" and the NIST **Equal Employment Opportunity Award** "for his concerted efforts in diversifying the Chemical Science and Technology Laboratory workforce" Charles Tilford also received the DOC **Gold Medal** "for leadership and technical contributions in establishing NIST's world-class programs on vacuum and low-flow-rate measurements and standards" Ray Radebaugh won the DOC **Silver Medal** "for the development of advanced low-temperature refrigeration systems" DOC **Bronze medalists** were Margaret Kline for "dedicated and exemplary work in the development of high-accuracy methods for characterizing amplified DNA," William MacCrehan "for his pioneering research in analytical separation science," and Patrick O'Hare "for development of NIST's fluorine combustion bomb calorimetric facility" The NIST **Applied Research Award** went to Stephen Stein "for technical innovations in implementation of mass spectrometric databases for use in commercial instruments" William Dorko and Franklin Guenther received the **Edward Bennett Rosa Award** "for establishing the infrastructure for commercial production of gas mixture standards with well-defined traceability to NIST" 1995 **Measurement Service Awards** went to Margaret Kline for the development of SRM 2391, PCR-Based DNA Profiling Standard, Robert Goldberg and Yadu Tewari for the Enzyme-catalyzed Biothermodynamics Database, J. Michael Hall for air speed calibration services, Greg Driver for primary pressure standards based on piston gauges, Marcia Huber for the development of OILTRAPP and updating of the REFPROP and SUPERTRAPP databases, and Jeanice Brown-Thomas and Katherine Sharpless for SRM development and quality assurance activities on fat-soluble vitamins and carotenoids in serum. The **CSTL Technical Achievement Award** went to Richard Cavicchi and Steve Semancik for their patented work on micro-hotplate array sensors.

Technical Highlights
In the following pages, recent activities and technical directions of the CSTL Divisions are highlighted.

I. Biotechnology Division (831)

Walter J. Stevens, Chief

A. Division Overview

The Biotechnology Division provides NIST with a cohesive effort to address critical measurement and data needs of the rapidly developing biotechnology industry. The mission of the NIST Biotechnology program is to advance the commercialization of biotechnology by developing the scientific and engineering technical base, reliable measurement techniques and data to enable U.S. industry to produce biochemical products quickly and economically with appropriate quality control. To accomplish this mission, the Division establishes a variety of long-range research programs to maintain critical technical expertise needed for the development of advanced measurement methods, standard reference materials and databases for use by industry and other research enterprises. The Division fosters collaboration among NIST scientists conducting biotechnology research, and raises the visibility of the NIST Biotechnology program, which leads to enhanced collaborations with industry, universities and other government agencies.

To plan and guide Division research programs effectively, Division scientists are active in many forums that provide feedback on long-term and short-term needs for biotechnology commercialization. These activities supplement the high level of Division participation in scientific meetings and topical workshops. For example, during FY95 the Division continued active participation in the Biotechnology Industry Organization (BIO), the ASTM Committee E-48 on Biotechnology, and the IUPAC Commission on Biophysical Chemistry. The Division worked with the NIST Advanced Technology Program (ATP) to plan a "Workshop on Tissue Engineering: From Basic Science to Products" (co-sponsored with FDA, NSF and NIH) in November, 1994. A "Biotechnology Strategic Planning Workshop", at which participants from industry and academe presented visions of the future of biotechnology and NIST's potential contributions, was held in December, 1994. Early in 1995, Division members participated in the planning of an ATP workshop on "Catalysis and Biocatalysis" that led to the establishment of an ATP focus program. Two Division members served on ATP Source Evaluation Boards that rank and select ATP award winners, and many Division members participated as reviewers for both general and focussed ATP competitions. Throughout the year, the Biotechnology Division continued to play a major role in the planning and coordination of Federal biotechnology research through membership in the Biotechnology Research Subcommittee (BRS) of the National Science and Technology Council (NSTC). The former Division Chief served as Chair of the BRS through July, 1995, and coordinated the publication of a major report entitled "Biotechnology for the 21st Century: New Horizons". The Division continues to play an active role in the organization and sponsorship of major scientific meetings. The Division co-sponsored (with DoE) an international meeting on the Critical Assessment of Techniques for Protein Structure Prediction that was held at Pacific Grove, California in December, 1994. Division scientists participated in the organization of the 50th Calorimetry Conference that was held at NIST in July, 1995.

The staff of the Biotechnology Division consists of 36 NIST employees and a comparable number of contract researchers, guest scientists, and postdoctoral fellows. During FY95, the Division was organized into four Groups: (1) DNA Technologies; (2) Bioprocess Engineering; (3) Structural Biology; and (4) Biosensor Technology. Several important managerial, budgetary, and organizational changes have occurred in FY95. In July, the Division Chief, Dr. Lura J. Powell, accepted a new position as Director of the NIST Advanced Technology Program. **Dr. Walter J. Stevens**, who had been Deputy Division Chief since the beginning of the fiscal year, became the new Chief in August. Also, during the summer of 1995,

NIST suffered a budget rescission which resulted in the postponement of many of the Division's plans for expansion. However, we were awarded a NIST competence-building project, beginning in FY 1996, for the development of a program in hybrid bilayer technology. These changes resulted in a recent reevaluation of the Division's research programs, and plans have been made to change the name of the Biosensor Technology Group to the **Biomolecular Materials Group** in FY 1996. The new name reflects the increased emphasis on bioactive surfaces, including the hybrid bilayer competence project. In addition to this new emphasis, the Group will continue to pursue research related to biosensor development and bioelectronics. In the summer of 1995, the University of Maryland received funds from the state legislature to expand the facility that houses the **Center for Advanced Research in Biotechnology** (CARB). The expansion, which will be complete in the summer of 1997, will more than double the available research space, and will allow the Division to expand its collaboration with the **University of Maryland Biotechnology Institute** (UMBI) for the measurement of protein structures and properties. The new building will include a special facility for state-of-the-art, high-field NMR instruments, which will play a central role in future NIST/UMBI development of protein structure measurement technology.

FY95 was a very productive year for scientists of the Biotechnology Division. A brief overview of each Group in the Division, and the highlights of several research programs are given below.

The **DNA Technologies Group** carries out research and standard reference materials (SRM) development in areas related to the detection and characterization of DNA. Methods and standards are being developed to characterize accurately DNA profiles for forensic and other human identification uses. This work has immediate impact on law enforcement agencies, the military, and the substantial private sector effort in human identification. In FY95, a new standard reference material was released, **SRM 2391**, which is a **Polymerase Chain Reaction-based DNA profiling standard** developed for the forensic and paternity testing communities. This is the second SRM developed by this group. The first, SRM 2390, is a key element required for the standardization and quality assurance of forensic testing using methods based on restriction fragment length polymorphisms (RFLP). In FY95, we designed and began the initial characterization of a third standard, **SRM 2392**, a **DNA Sequencing Standard,** which is needed for quality assurance in the growing commercial applications of DNA sequencing. The prototype SRM 2392 contains several important elements, including a specific mitochondrial DNA sequence to assure accurate human identification by sequencing, and a synthetic challenge sequence for maintaining quality assurance with automated DNA sequencers. We believe the development of such essential reference materials and expanding the technical expertise to produce them are key elements in successfully maintaining US leadership in genomic technology. In addition, research aimed at future SRM development will be focused on the use of DNA in diagnostic measurements for disease detection using methods such as DNA immobilization on microchips. Long-range research in the Group includes the development of methods for detecting and quantifying DNA damage and repair, processes that are critical to understanding the genesis of cancer. Methods have been developed to characterize DNA damage on a molecular scale at levels approaching one base per million using GC/MS techniques, and recently these methods have been used to study the kinetics and specificity of DNA repair by specific enzymes.

The **Bioprocess Engineering Group** is focused on the development of measurement methods, databases, and generic technologies related to the use of biomolecules and biomaterials in manufacturing. In FY95, researchers in the Group completed a comprehensive, evaluated **database on the thermodynamics of enzyme-catalyzed reactions**. This database provides critical information to scientists and engineers engaged in both research and development of biocatalysis for chemical manufacturing. The data can be used to optimize existing processes and to evaluate proposed processes. In FY 1996, the database will be made easily accessible to scientists by putting it on the World Wide Web. A major new effort for the Group in FY95 was the development of a research program aimed at the unique potential of the hydroxylase class of enzymes for chemical

manufacturing. The research is focused on solving technical roadblocks through the use of state-of-the-art measurements and advanced modeling methods to characterize biocatalysts and molecular processes. Proof-of-principle experiments, involving electrode-driven redox chemistry incorporating the **cytochrome P450 enzyme system,** are being studied as the basis of controlling bio-synthetic reactions. Success in this area involves finding generic routes for meeting the energy requirements of these enzymes and on developing synthetic methods of carrying out cell functions such as electron transfer between proteins. Other research in this group includes new chromatographic processes for separating biomolecules from fermentation broths. During FY95, a NIST-developed **electrochromatography** method has been evaluated for the separation of DNA and viral particles from proteins. This research has resulted in a patent disclosure for this promising separation method.

The **Structural Biology Group** is located at the **Center for Advanced Research in Biotechnology** (CARB) on the University of Maryland Shady Grove campus about four miles from NIST. CARB is a joint collaboration of the Biotechnology Division and the University of Maryland Biotechnology Institute. Scientists at CARB develop and apply measurement methods, databases, and state-of-the-art modeling methods to advance the understanding of protein structure/function relationships. X-ray and NMR methods are used to measure the structures of prototypical proteins, enzymes, enzyme-substrate complexes and other macromolecular systems. Structural information is combined with molecular biology and physical measurement methods including calorimetry and spectroscopy to understand and control structure/function relationships such as thermodynamic stability, the energetics of protein folding, protein substrate interactions and enzymatic reaction pathways. Highlights for FY95 include a recently released, on-line version of NIST Standard Reference Database 21, the **NIST/NASA/CARB Biological Macromolecule Crystallization Database** (BMCD). The widely used BMCD contains crystal data, protocols and results of crystallization experiments, including those undertaken in the microgravity environment of space flight. The on-line version provides a sophisticated user interface that allows browsing, searching, downloading and displaying the data. The data are used by crystallographers to develop crystallization strategies for newly discovered biological macromolecules and to reproduce crystallization protocols for existing molecules. Other research at CARB includes the development of **Computational chemistry** methods to model the energetics and energy profiles of enzyme-catalyzed reactions. Recent results include the application of **new reaction-field methods** to study enzyme mechanisms such as the hydrolysis of phosphate esters by Ribonuclease A. Modeling methods such as these are important to the pharmaceutical industry for drug design, and will play an increasing role in the engineering of enzymes for specific purposes. CARB is involved in a number of cooperative research and development agreements (CRADAs) with industry. The latest agreement is with Dupont Merck Pharmaceuticals for the validation of modeling methods for the prediction of protein/substrate recognition and binding affinity. Our continued success in this field is an outgrowth of a five-year competence building program in computational biotechnology.

The **Biosensor Technologies Group** develops generic measurement technologies, utilizing both optical and electrochemical approaches, for applications in clinical diagnostic measurements, bioprocessing, and environmental monitoring. During the latter part of FY95, the Group was awarded a new NIST competence-building project (Dr. Anne Plant, Champion) for research on **hybrid bilayer membranes** as biomimetic materials. This research and other ongoing work on membranes imbedded with **self-assembling pore proteins**, comprise a research program in bioactive surfaces that has long-range importance to biosensing, bioelectronics, and bioprocessing. In the area of biomolecular electronics, the light-sensitive protein, **bacteriorhodopsin** (bR), is being studied for use in imaging technology and as a potential approach to the storage and retrieval of high-density information. Recent work in this area includes the preparation of a special tin-oxide-coated antimony electrode that, when coated with bR, allows the direct measurement of protons being pumped as part

of the photon-initiated signal transduction by the protein. This new measurement method will allow the direct measurement of the performance of engineered bR mutants and chemically-modified retinal cofactors that may be used to shift the light-absorption profile of the protein. The Group also carries out more applied research aimed at **developing and optimizing biosensors**. The **Consortium for Advanced Biosensors** (CAB) was established in April, 1993, to address the needs of industry for the development of measurement technology based on biomolecules and bioactive layers. Over the past two and a half years, the consortium has sponsored research to address the problem of nonspecific binding of proteins to surfaces, which is one of the major impediments to biosensor development. CAB began with seven industrial members and two Federal agency members (including NIST). However, recent reorganizations and downsizings have resulted in the withdrawal of several industrial members. Thus, during FY95, the consortium membership has fallen below the number necessary to sustain a viable research program. CAB will be reevaluated in the early part of FY96. If new industrial members are not found, the consortium is likely to be terminated in favor of individual cooperative research and development agreements (CRADAs).

Meeting the future needs of the biotechnology industry will require the strengthening of existing Division programs and the development of technical expertise in new areas. Included in Division plans are the continued expansion of programs in biomolecular materials, which reflects and emphasis on generic needs common to many kinds of surfaces and materials that are components in sensors, processing, diagnostics, and other applications. The expansion of the DNA technologies effort to include measurement tools and quality assurance standards for DNA diagnostic measurements is certainly a high priority, given the rapid growth of industrial applications in this area. At CARB, upgrading the existing X-ray crystallography facility and establishing a state-of-the-art NMR facility in collaboration with the University of Maryland are high priorities. This is a reflection of the importance of biomolecular structures in the future development of biotechnology, particularly in pharmaceutical development and biomanufacturing.

Throughout the Division, expanded emphasis will be placed on the development of modeling which relates molecular structure to the properties of biomolecules, biomaterials, and bioprocesses. The use of biological macromolecules in non-biological applications such as chemical manufacturing and environmental bioremediation continues to be a promising area of biotechnology. The Division will continue to build expertise in bioprocess technology, with an emphasis on measurements and data to help industry solve generic problems that limit technology development. As the Division gains more experience with the development and implementation of on-line databases, efforts will be expanded in the area of bioinformatics, which is the development of computational methods for using large biomolecular structure and sequence databases to identify, analyze or predict the structure and/or function of new biomolecular species. This will enhance our own research programs and also aid industry in the efficient use of chemical and biochemical data in the development of new products and processes.

B. Selected Technical Reports

1. *SRM 2391, PCR-based DNA Profiling Standard Released for Forensic and Paternity Testing Laboratories*

M.C. Kline, J. Redman, and D.J. Reeder

Objective: To provide well-characterized materials intended for use (1) in the standardization of forensic and paternity quality assurance procedures for Polymerase Chain Reaction (PCR)-based genetic testing and (2) for instructional law enforcement or non-clinical research purposes within the domain of human identity.

Problem: Human identity testing using PCR-based technologies has been growing rapidly. With this growth comes a need for accurate interlaboratory exchange of information. For typing information to be easily exchanged, either methods of analysis must be identical or common reference standards must be available. PCR technologies are diverse. For example, in a recent interlaboratory study involving 25 laboratories, we observed the use of five different amplification methods and the use of five different electrophoretic gel matrices for typing the D1S80 genetic locus. Since then, advances in technologies now allow the rapid detection of the amplified products through post electrophoretic staining with silver or fluorescent dyes. Even more sensitive, real-time analysis is achieved by tagging the amplified product with fluorescent primers.

Approach: Release Standard Reference Material (SRM) 2391 PCR-based DNA Profiling Standard to: 1) provide laboratories with materials they can use to validate their methods and be able to compare results with other laboratories for many different genetic loci, and 2) assure that the materials selected are stable under possible deleterious thermal conditions that could occur during shipping.

Results and Future Plans: Standard Reference Material (SRM) 2391 PCR-based DNA Profiling Standard was released in June 1995. Work in the months prior to the SRM release involved a complete re-characterization of the materials by us and by the Armed Forces DNA Identification Laboratory (AFDIL).

The SRM 2391 certificate included not only the certified values for the genetic locus D1S80, but also a set of information values for the following genetic loci for the genomic DNA sets in the SRM: HLA-DQα, LDLR, GYPA, HBGG, D7S8, GC, HUMTH01, and HUMF13A01. Additional information values for the genetic loci HUMVWFA31 and HUMFES/FPS were supplied for the cell lines. Additionally, we investigated SRM 2391's stability at room temperature. We found that SRM 2391 was stable for at least seven days at 22 °C, whereas the suggested storage temperature is -20 °C, thus demonstrating the robust nature of the materials.

Future plans include adding additional genetic locus information to the SRM certificate for the genomic DNA in the SRM and increasing the number of genetic loci to add as information values. Currently no commercial product is available to supply DNA samples with genomic typing information for multiple loci. Adding additional locus information to the certificate should be beneficial to human identity laboratories.

Publications:

Reeder, D.J., Kline, M.C., and Richie, K.L., "**An Overview of Reference Materials Prepared for Standardization of DNA Typing Procedures**." Fres. J. Anal. Chem. 352:246-249 (1995).

2. *Interlaboratory Testing and Development of Prototype Reference Materials for Mitochondrial DNA Sequencing*

***B.C. Levin**, K.H. McKenney, P. Reddy, K.L. Richie, and D.J. Reeder*

Objective: To develop human mitochondrial DNA (mtDNA) standard reference materials (SRMs) which will help the forensic, medical, and industrial communities in the areas of diagnostics and human identification.

Problem: MtDNA is being used by the forensic community for human identification and by the medical community for diagnoses of a number of human diseases now known to be associated with specific mutations of mtDNA. Standard Reference Materials for mtDNA will help forensic analysts and medical researchers satisfy their quality assurance needs for sequencing.

Approach: Forensic and medical communities compare the mtDNA sequence of interest in their test subjects with published human mtDNA sequences. For forensic use, two hypervariable regions in the non-coding region of the mtDNA D-loop (termed HV1 and HV2) provide sufficient information to allow almost unique individualization of a small sample of tissue or bone. We are developing mtDNA standard reference material sets to allow quality DNA sequencing. Our first interlaboratory evaluation (ILE) was designed to assess the ability of forensic laboratories to give the same DNA sequence results for a mtDNA test sample and to correctly match two of the three samples. The mtDNA samples consisted of a set of blood samples from a parentage trio. Two of the samples had the same sequence while the third type was different. Laboratories were asked to extract, amplify and sequence mtDNA samples using their own protocols and to report their results. Fifteen laboratories participated in this study, eleven of which reported data and called the correct match between the paired mtDNA samples. We suggested recommendations for better nomenclature and for more uniform reporting procedures. A second ILE consisted of sending selected DNA samples to non-forensic DNA sequencing laboratories to assess their ability to sequence sets of complex DNA sequences. Ten laboratories participated by sending data and results to NIST for analysis. We determined that, in general, that all laboratories satisfactorily determined the sequence of one strand of JT3, and all labs had difficulty determining the complementary strand of JT3. In-house research is being conducted to assure that each step of the DNA sequencing process is reliable, simple and efficient and that the components of the SRM will provide reliable sequencing results. The concluding step will be to conduct a final ILE of the SRM for the entire mtDNA. Improvements based on the results of this interlaboratory evaluation can then be made before the SRM becomes available.

Results and Future Plans: For forensic use, we have produced a cloned region of HV1 called JT3, and a cloned region HV2 is being prepared in a similar manner. Further, a lymphoblastoid tissue culture cell line for development of a mtDNA SRM has been characterized and tested. Compared to the Anderson sequence, the lymphoblastoid tissue culture cell line has no differences in the HV1 region and only two differences in the HV2 region. For sequencing the entire mtDNA sequence, forty-eight sets of unique primers have been identified and could be included with the SRM. These sets are being tested to assure that they will correctly amplify and sequence any mtDNA area of interest. Before release, an ILE of the mtDNA SRM cloned HV1 and HV2 materials, as well as the cell line characterized for the entire 16,569 base pair sequence, will be conducted by multiple laboratories.

Publications:

McKenney, K., Hoskins, J., Tian, J., and Reddy, P., "**DNA Molecules as Standard Reference Materials I: Development of DNA Identification Sequences and Human Mitochondrial DNA Reference Sequences,**" J. Res. NIST (Accepted for Publication).

3. *Confirmation of Heteroplasmy in Mitochondrial DNA*

B.C. Levin and H. Cheng (Geo-Centers, Inc.)

Objective: To determine if mitochondrial DNA (mtDNA) from one individual represents a homogeneous or heterogeneous population of DNA molecules.

Problem: Each human cell can have a few dozen to several thousand molecules of mtDNA. Sequence analysis of mtDNA is being used for human identification and is primarily based on the considerable sequence variation between individuals found in the two hypervariable regions (HV1 and HV2) located in the non-coding displacement loop (D-loop). PCR amplification and sequencing of the mtDNA product of these regions have been generally successful. Some individuals, however, contain long homopolymer stretches of only cytosine bases (C-stretch). The presence of the C-stretch interferes with the sequence analysis in the region following the C-stretch, thus presenting problems to laboratories that use mtDNA for human identification. The initial objective of this research was to try different polymerases, additives, and conditions to determine if these changes would permit sequencing this difficult region. The results of this initial research indicated that these changes did not solve the problem. The extremely clear electropherograms obtained with the new enzymes and additives suggested, however, that the problem of sequencing beyond the C-stretch may be due to the presence of different numbers of cytosine residues in the C-stretch of the individual.

Approach: The hypothesis of heteroplasmy was tested by capillary electrophoresis (CE) of the amplification products. The CE showed that control DNA (no C-stretch problem) generated a symmetric peak indicating a single PCR product, whereas the DNA products with the C-stretch problem produced a shoulder peak indicating more than one product. These results substantiated the hypothesis that the C-stretch problem is due to a heteroplasmic mixture of mtDNA's, each containing a different number of C's. To examine this hypothesis further, the PCR product of this region was cloned. The mtDNA sequence of 19 clones showed four had 11 C's, twelve had 12 C's, and three had 13 C's. In addition, the area following the C-stretch was sequenced without problems when one used the cloned DNA as the template. The conclusion from this series of experiments is that the PCR product is a heteroplasmic population.

Results and Future Plans: We now needed to determine whether the heteroplasmy seen in clones from the PCR product is an artifact of the PCR process or if the mitochondrial population itself is heteroplasmic. A second round of PCR on the DNA cloned from the PCR product again generated the problem of unclear sequence in the region following the C-stretch. This result confirmed that the PCR process itself introduces heteroplasmy. To determine if heteroplasmy exists in the mtDNA of the individual, we needed to directly clone the mtDNA from the cells rather than the PCR product. A large quantity of cells was required for these experiments and a human tissue culture cell line with the C-stretch was developed. Total DNA was isolated and the mtDNA was separated on a column. Restriction enzymes were found that cut the mtDNA HV1 region in an area away from the replication origin. The DNA fragments were separated on an agarose gel and the area of the gel containing the mtDNA of the correct size was isolated and the DNA was cloned. The DNA sequence from 19 clones showed that two had 10 C's, six had 11 C's, nine had 12 C's and two had 13 C's. These results indicate that heteroplasmy does exist in the human mtDNA population. Future plans include repeating these experiments with another tissue culture cell line which also contains the C-stretch and with mtDNA from fresh blood to ensure that the heteroplasmy does not result from growth under cell culture conditions.

Publications:

Levin, B.C., Cheng, H., O'Connell, C., Reeder, D.J., and Holland, M., **"Evaluation of Alternative Enzymes and Additives to Improve Sequencing of Mitochondrial DNA,"** Proceedings of the Fifth International Symposium on Human Identification, 1994, Promega Corporation, 1995, p. 170.

4. *Novel Activities of Human Uracil DNA N-glycosylase for Products of Oxidative DNA Damage*

***M. Dizdaroglu**, A. Karakaya (Univ. of Ankara, Ankara, Turkey), and P. Jaruga (Medical Academy, Bydgoszcz, Poland)*

Objective: To test the hypothesis that DNA repair enzyme human uracil DNA *N*-glycosylase may recognize some products of oxidative DNA damage and excise them from DNA.

Problem: Human uracil DNA *N*-glycosylase is a DNA repair enzyme that recognizes uracil and excises it from DNA. A major function of this enzyme is to protect cells from premutagenic uracil resulting from deamination of cytosine in DNA. Many DNA repair enzymes possess multiple activities for modifications in DNA. For this reason, human uracil DNA *N*-glycosylase may also have an activity for lesions that are formed in DNA by oxidative damage.

Approach: Oxidative damage by free radicals generates a myriad of base modifications in DNA. Precise identification and quantification of these lesions are achieved by the methodologies incorporating the GC/MS technique, which were developed in our laboratory. Because of its ability to measure numerous DNA products at the same time, this technique permits the study of the substrate specificity of a DNA repair enzyme toward a multitude of DNA base modifications under the same conditions. In addition, kinetics of product excision can be determined. We employed this unique approach to test whether human uracil DNA *N*-glycosylase possesses any activity for base modifications in oxidatively damaged DNA.

Results and Future Plans: DNA substrates were prepared by γ-irradiation of DNA. These were incubated with active human uracil DNA *N*-glycosylase, heat-inactivated enzyme or buffer. DNA was ethanol-precipitated. Supernatant fractions after derivatization, and pellets after hydrolysis and derivatization were analyzed by GC/MS. The results demonstrated that human uracil DNA *N*-glycosylase excised the uracil derivatives isodialuric acid, 5-hydroxyuracil and alloxan from DNA. These compounds are formed by hydroxyl radical attack on cytosine in DNA. Kinetics of excision were also determined. The excision of these uracil derivatives is consistent with the recently described mechanism for recognition of uracil by human uracil DNA *N*-glycosylase. Nine other products that were identified in DNA samples were not substrates for the enzyme. The results indicate that human uracil DNA *N*-glycosylase may have a function in the repair of oxidative DNA damage.

Removal of individual products from cellular DNA by cellular repair in human cells will be studied in FY96. Kinetics of repair will be determined. This work may contribute to the understanding of cellular repair of oxidative DNA damage in terms of individual DNA base products.

5. *Measurement of ^{60}Co-γ-Ray Induced DNA Damage by Capillary Electrophoresis*

Z. Nackerdien and D.H. Atha

Objective: Capillary electrophoresis is being developed as an alternative analytical tool for the measurement of radiation-induced damage to bacterial and human DNA.

Problem: Ionizing radiation produces a spectrum of DNA damage ranging from base lesions to strand breaks and crosslinks. Novel tools that can augment existing analytical methods are crucial in understanding the chemical nature and DNA fragmentation processes associated with radiation-induced damage.

Approach: Capillary electrophoresis (CE) is a relatively new tool which has been used with success in the fields of analytical chemistry, pharmacology, forensic sciences, and molecular biology. Its enhanced resolution, speed, sensitivity, and reproducibility over slab gel electrophoresis have been used to great advantage in applications such as the study of human diseases, DNA sequencing, and the sizing of DNA fragments.

Results and Future Plans: During FY95, we used CE to monitor ^{60}Co-γ-ray-induced damage to a 1 kb DNA ladder, which consists of restriction fragments ranging from 75-12000 bp. DNA samples were exposed to graded doses of ^{60}Co-γ-rays in the presence and absence of a fluorescent dye, ethidium bromide (EB). The analysis showed peak broadening without significant changes in the size distribution of irradiated fragments. Radiation-induced conformational changes may account for this peak broadening. EB addition caused small increases in the retention times of DNA fragments without affecting the overall DNA damage. This indicates that the presence of intercalated EB during radiation will not stabilize the DNA against ^{60}Co-γ-ray-induced damage.

These results are the first CE measurements of ^{60}Co-γ-ray-induced DNA damage at the level of 60 Gy in double-stranded DNA fragments. We have identified conformational changes associated with radiation-induced damage which can be attributed to strand breaks that are not prevented by the addition of ethidium bromide. These results will provide the groundwork for the interpretation of natural DNA fragmentation processes in plasmids and human cells.

In FY96, DNA damage in linear and circular, plasmid DNA will be studied by CE. The sensitivity of this method will be optimized using different polymers and fluorescent dyes. Such new methods will be needed by industry to efficiently assess plasmid integrity. This is critical in the commercial production of recombinant DNA libraries.

6. *Electro/Optical Probing of Proteins on Modified Metal Electrodes*

A.K. Gaigalas, V. Reipa (UCLA), L. Wong (UCLA), W. Yap, G. Niaura (Vilnius State Univ., Vilnius, Lithuania), A. Roitberg (Geo-Centers, Inc.), and V.L. Vilker

Objective: Measure the structural changes occurring in proteins during redox processes on modified electrodes. Measure electron transfer rates associated with the redox processes. Develop models to correlate the experimental results.

Problem: Commercial application of redox enzymes is hampered by a lack of data and models of intra- and inter-protein electron transfer rates, and of inexpensive and reliable sources of reducing power. This work will provide a rational scheme for the design and implementation of multiprotein redox enzyme systems, and allow for development of sources of reducing power based on modified electrodes.

Approach: Electrochemical measurements, surface enhanced Raman spectroscopy (SERS), electroreflectance (ER), and spectroellipsometry (SE) are being used to characterize the electrode surface and measure the electron transfer (ET) to several redox proteins (e.g., putidaredoxin (Pdx), azurin, cytochrome c). Linear sweep voltametry (LSV) provides a diagnostic technique for the general suitability of the entire system. SERS provides molecular-level information about structural changes that proteins undergo during changes in oxidation state, as well as structural signatures of electrode-modifying layers. ER provides means to determine ET kinetics and to evaluate the importance of specific protein parameters controlling these rates. *In situ* characterization of the electrode/solution interface is rendered by SE in conjunction with electrochemical techniques.

Results and Future Plans: SERS has been used to identify metal site vibrations in cytochrome c, Pdx and azurin. These can be used to monitor the redox process from proteins on adsorbed layers. ER has been successfully applied to the measurement of the nuclear and electronic contributions to the ET rate. The effects of electrode modification, such as neutralization of repulsive electrostatic charge, on the ET rates have been reported. SE has demonstrated the existence of stable protein layers on bare and modified electrodes. Comparison of the LSV and ER results indicate simultaneous occurrence of two redox processes: one from adsorbed proteins and the other from proteins in solution. The ET process in the latter case occurs through the layer of adsorbed proteins.

A sufficient amount of experimental results have been accumulated to warrant an effort to model and correlate these results. A computational chemist will be joining this effort, initially to develop a detailed calculation of the nuclear factor in ET, separating the metal site contributions from those due to the rest of the protein. We have gained more insight of how to combine the results from the various experimental techniques. More of the combined measurements will be performed on azurin and plastocyanin.

Publications:

Reipa, V., Gaigalas, A.K., Edwards, J.J., and Vilker, V.L., **Surface-enhanced Raman Spectroscopy (SERS) Evidence of Charge Transfer Between Putidaredoxin and a Silver Electrode,"** J. of Electroanalytical Chem. 396, 299-303 (1995).

Wong, L.-S. and Vilker, V.L., "**Direct Electrochemistry of Putidaredoxin at a Modified Gold Electrode,"** J. of Electroanalytical Chem. 389, 201-203 (1995).

Wong, L.-S., Vilker, V.L., Yap, W.T., and Reipa, V., **"Characterization of Mercaptoethylamine-modified Gold Electrode Surface and Analyses of Direct Electron Transfer to Putidaredoxin,"** Langmuir (in press).

7. *Thermodynamics of Enzyme-Catalyzed Reactions*

R.N. Goldberg, Y.B. Tewari, M.V. Rekharsky, and V.L. Vilker

Objective: The aim of our research is to study the thermodynamics of reactions which can benefit biotechnology.

Problem: A knowledge of the position of equilibrium is essential for the optimization of industrial processes. Reaction conditions such as temperature, pH, ionic strength, and co-factor concentrations can substantially affect the position of equilibrium of many biochemical reactions.

Approach: The accomplishment of this research relies upon a combination of techniques: chromatography, microcalorimetry, thermodynamic modeling, and effective utilization of results in the literature. This combination allows for checks on the consistency of the measurements and for the development of suitable thermodynamic models. This frequently allows one to make reliable extrapolations of the data outside of the region in which actual measurements have been performed. The microcalorimetric capability has been particularly important in allowing for the extrapolation of data to higher temperatures. This effort has also resulted in the development of estimation schemes based upon limited and carefully chosen sets of data.

Results and Future Plans: We have completed a series of reviews on the thermodynamics of enzyme-catalyzed reactions. The entries in these reviews follow the order used by the International Union of Biochemistry and cover all six major classes of enzymes: oxidoreductases, transferases, hydrolases, lyases, isomerases, and ligases. Chemical Abstract Service registry numbers have been assigned to the reactants. Also, there is a cross reference between the reactants and the Enzyme Commission numbers of the enzymes used to catalyze the reactions. We plan to make this database available on the World Wide Web.

We have also completed a series of experimental studies using non-aqueous solvents as well as the first thermodynamic study of a reaction catalyzed by the oxygenase subclass of enzymes. Plans call for the completion of a study of representative (NAD + NADH) coupled reactions, the reactions used for the manufacture of cyclodextrins and ascorbic acid, and, possibly, reactions involving the enzymatic hydroxylation of aromatic hydrocarbons.

Publications:

Goldberg, R.N. and Tewari, Y.B., **"Thermodynamics of Enzyme-catalyzed Reactions: Part 3. Hydrolases,"** J. Phys. Chem. Ref. Data 23, 1035 (1994).

Tewari, Y.B., Schantz, M.M., Pandey, P.C., Rekharsky, M.V., and Goldberg, R.N., **"Thermodynamics of the Hydrolysis of N-acetyl-L-phenylalanine Ethyl Ester in Water and in Organic Solvents,"** J. Phys. Chem. 99, 1594 (1995).

Goldberg, R.N. and Tewari, Y.B., **"Thermodynamics of Enzyme-catalyzed Reactions: Part 4. Lyases,"** J. Phys. Chem. Ref. Data (in press).

Goldberg, R.N. and Tewari, Y.B., **"Thermodynamics of Enzyme-catalyzed Reactions: Part 5. Isomerases and Ligases,"** J. Phys. Chem. Ref. Data (in press).

Tewari, Y. B., Schantz, M. M., Rekharsky, M. V., and Goldberg, R. N., **"Thermodynamics of the Hydrolysis of 3,4,5-trihydroxybenzoic Acid Propyl Ester (n-propylgallate) to 3,4,5-trihydroxybenzoic Acid (gallic acid) and Propan-1-ol in Aqueous Media and in Toluene,"** J. Chem. Thermodyn. (in press).

8. *PreparativeElectrochromatographic Separations of Nucleic Acids*

K.D. Cole

Objective: To develop new high resolution techniques to purify large amounts of nucleic acids.

Problem: Large scale purifications of nucleic acids are necessary to meet the needs of research and development laboratories and for uses as new classes of therapeutic agents. A large number of human gene therapy clinical trials are currently underway. A variety of methods for introducing DNA into cells and tissues are being tested including the use of viruses, cationic liposomes, DNA-protein complexes, and direct injection of DNA. Oligonucleotides designed to inhibit the expression of specific genes show promise as antiviral and anticancer agents. Nucleic acid molecules selected from combinatorial libraries that are capable of high affinity binding to target molecules are examples of ligands that could be used therapeutically or for diagnostic purposes. Production of large amounts of DNA for these types of experiments is a new challenge in bioprocessing.

Approach: Electrophoresis has proven to be a highly successful method for the separation of nucleic acids on an analytical scale. Electrophoresis in gels and capillaries are high resolution analytical methods, but they are difficult to scale up. Electrochromatography (EC) might be a suitable method to scale up the electrophoresis of nucleic acids. EC is the application of an axial electrical field to a chromatography column.

Results and Future Plans: We used bacteriophage λ DNA, supercoiled plasmid DNA, and a mixture of DNA restriction fragments to determine the utility of EC for the separation and purification of nucleic acids. DNA was retained by relatively low negative electrical fields (electrophoresis opposing buffer flow) in a column packed with porous chromatography media. A field of the opposite orientation was not effective at retaining the DNA. The electrical field strength required to retain the DNA was dependent upon the buffer flow rate and the porosity of the packing material. A large volume of a dilute DNA solution was concentrated at the inlet of the chromatography bed by an electrical field and buffer flow. DNA was size-fractionated by varying the electrical field strength and flow rate. At a given electrical field strength and flow rate, lower molecular weight DNA restriction fragments were not as strongly retained as higher molecular weight fragments. By selecting a specific set of conditions (packing material, flow rate, and electrical field strength) the molecular weight of DNA fragments retained by the column was adjusted. Improved electrochromatography fittings were developed that allow a uniform and reliable electrical field to be applied to a chromatography column.

We plan to extend work on virus concentration and purification based on encouraging result using the bacteriophage, M-13. Separation of different forms of plasmid DNA are being studied as well as lower molecular weight DNA (oligonucleotides).

Publications:

Cole, K.D., **"Concentration and Size-Fractionation of Nucleic Acids and Viruses in Porous Media,"** Patent filed November 1995.

Cole, K.D. and Cabezas, H., Jr., **"Electrochromatography Apparatus,"** Patent filed November 1995.

9. *NMR Studies of Structure and Dynamics of Metalloproteins*

B. Coxon, M. Holden (Geo-Centers, Inc.), and Nese Sari (Bogazici Univ., Istanbul, Turkey)

Objective: High resolution NMR spectroscopy will be used to investigate the structure and dynamics of metalloproteins, particularly those of the ferredoxin group; for example, the oxidized form of putidaredoxin (Pdx).

Problem: Although the iron-sulfur cluster in ferredoxin proteins is thought to play a key role in the electron transfer processes that control the enzymatic activity of these proteins, little is known about the immediate electronic and structural environment of the iron-sulfur cluster. This region has proved to be inaccessible to high resolution proton NMR because of severe broadening of the proton resonances by the paramagnetic metal cluster.

Approach: One-dimensional (1D) and two-dimensional (2D) homo- and hetero-nuclear NMR methods will be applied to proteins uniformly labeled, or specifically labeled, with carbon-13 and/or nitrogen-15. Because the magnetic moments of these isotopes are approximately four and ten times smaller, respectively, than the proton moment, the NMR signals of such isotopes (when observed directly) are expected to be correspondingly less broadened by the paramagnetic iron-sulfur cluster, and, therefore, should reveal more structural information about the cluster region than proton NMR. Another part of our strategy involves proton NMR spectroscopy in a region at much lower field than the usual proton range, in an effort to detect proton signals that are both highly paramagnetically broadened and shifted.

Results and Future Plans: During FY95, solutions of Pdx in 10% deuterium oxide were studied by 1D proton NMR at 400 MHZ and 1D and 2D proton NMR at 500 MHZ. The latter investigation involved the use of the 2D DQF COSY, NOESY, ROESY, and TOCSY techniques. The fingerprint cross peak patterns in the 2D DQF COSY and NOESY spectra were essentially identical with those in digital copies of data obtained in a cooperative arrangement with Professor T. Pochapsky of Brandeis University, thus confirming the identity of NIST prepared material with that reported in the literature. However, our NMR studies indicated that the protein contained a glycerol contaminant that originated from humectant present in the membrane filters used for processing. The isolation procedure has now been adjusted to eliminate this artifact.

Pdx, uniformly labeled with nitrogen-15, is being purified from an *E. coli* clone. This clone is expressing the Pdx protein in a defined medium, in which the sole source of nitrogen is ammonium chloride-^{15}N. We plan to study the iron-sulfur cluster region of the protein by nitrogen-15 NMR, using the direct observation technique. 2D proton-nitrogen-15 chemical shift correlation methods by both direct and indirect detection will be used to distinguish the different types of nitrogen functions, making use of the known proton NMR assignments for approximately 100 of the 106 amino acid residues in Pdx. These studies will be augmented by measurements of nitrogen-15 spin-lattice relaxation times and spectral linewidths, which have the potential for defining the distances of various nitrogen sites from the iron-sulfur cluster and the motional dynamics of various domains in the protein.

In later work, we plan to isolate carbon-13 labeled versions of Pdx and to study its structure using high-resolution carbon-13 NMR, by direct observation. In order to avoid the spectral complexity that could result from homonuclear, carbon-13--carbon-13 spin-spin coupling over one bond, the carbon-13 isotopic enrichment would be increased only to a level of 10%, thus giving a 1% probability on average, that adjacent carbon sites would each be labeled with the carbon-13 isotope. These heteronuclear NMR studies are expected to illuminate facets of protein structure that are not accessible by proton NMR.

10. Functionalization of Redox Proteins for In-Vitro Biocatalysis

J. Edwards, M. Holden (Geo-Centers, Inc.), and M. Mayhew (Geo-Centers, Inc.)

Objective: To use non-denaturing electrophoretic and chromatographic separations to enhance yield and speed of purification for redox proteins plastocyanin and putidaredoxin. The purified proteins will be chemically and genetically modified so that alterations in structure can be functionally evaluated with respect to stability, and biocatalytic efficiency.

Problem: The transfer of electrons in living cells is controlled by highly regulated oxidation-reduction (redox) reactions. Plastocyanin (Pcy) and putidaredoxin (Pdx) transfer electrons by oxidation-reduction reactions involving copper and iron metal centers, respectively. The protein systems involved in the regulation of electron transfer are not well understood, especially from a structural viewpoint. For functional studies and for the preparation of chemically modified proteins, highly purified native starting material is required. With proteins such as plastocyanin occurring in amounts as low as one part in 10,000 on a weight basis, isolation of useful amounts of highly purified material is technically difficult.

Approach: High resolution techniques such as chromatofocusing and free-solution isoelectric focusing will be used to obtain milligram quantities of material. Chemically and genetically modified forms (polymers, substituted metals, etc.) that may lead to altered stability and activities, will be constructed using various methodologies for polymer formation (e.g., glutaraldehyde and chondroitin sulfate) and metal substitution. The products will be characterized by analytical methods (one- and two-dimensional gel electrophoresis, free-solution electrophoresis) for determination of polymer number, pI, molecular mass and for any preparation artifacts.

Results and Future Plans: During FY95 we studied Pcy and Pdx with respect to new approaches for purification (e.g., metal ion affinity chromatography) and characterization (two-dimensional gel electrophoresis). We also began the production and characterization of chemically crosslinked polymers for both Pcy and Pdx. Spectroscopic studies (SERS) on purified preparations of the native proteins were begun.

In FY96, we intend to concentrate our efforts on using high resolution techniques to produce and more efficiently purify Pcy and Pdx. Also, the chemical modification of purified Pcy and Pdx will be evaluated for stability and biocatalytic activity. The initial modifications include the construction of polymeric forms (i.e., dimers, trimers, etc.) and the substitution of metals such as Zn(II), Co(II), and Ni(II) into the metal center to replace Cu(II) and Fe(II). The role these modifications play in protein stabilization and activity will be evaluated.

11. *Theory of Non-Covalent Protein-Ligand Binding*

M.K. Gilson and J.A. Given (CARB/Univ. of Maryland)

Objective: To understand the physical chemistry of specific, non-covalent binding of small molecules by proteins, and to incorporate this understanding into predictive computer models.

Problem: The specific binding of small molecules by proteins is of central importance in enzyme function and drug action. However, the mechanisms of this phenomenon are not fully understood. Predictive models for binding would be of great practical value in applications such as altering the substrate specificity of enzymes, and structure-based drug design.

Approach: Models for non-covalent binding typically possess two major components: a method for generating possible bound conformations for the protein-ligand complex, and an energy function for predicting the stability of a given complex. A number of energy functions have been described in the literature. However, it is not clear how well they work. A goal of the present project, therefore, is to develop and apply methods for testing the energy functions used in modeling protein-ligand interactions.

Results and Future Plans: A novel approach to testing energy functions has been developed. Given a protein-ligand complex whose conformation is known from experiment, and an artificially generated collection of plausible, but incorrect, conformations of the complex, an accurate energy function should assign the lowest energy to the correct conformation. An algorithm that generates plausible, but incorrect, conformations has been developed. It has three basic steps: 1) randomization of the ligand conformation and orientation, independently of the protein; 2) placement of the ligand at an arbitrary spot in the known binding site; and 3)optimization of the structure to a local energy-minimum. The algorithm has several novel features that will be described in a paper currently in preparation. The method is being used to test various models for long-ranged electrostatic interactions. One clear-cut result of this work is that much greater accuracy is achieved when all long-ranged interactions are included; i.e., when "cutoffs" are not used. In FY96, several simple energy functions will be characterized in studies of enzyme-inhibitor complexes of known structure. Tentative plans also call for the parallelization of this algorithm to permit efficient calculations on the IBM SP2 at NIST.

Computing the binding constant means computing a standard free energy. A rigorous formula for the free energy of binding, based upon classical statistical thermodynamics, has been derived. A paper in preparation will describe this derivation, and its implications for the computation of binding constants and the interpretation of experimental data. The concepts underlying the derivation have been used to establish a series of approximate but computationally tractable methods for estimating free energies of systems with modest numbers of rotatable bonds. Preliminary tests of these approaches have been promising. In FY96, their accuracy will be tested in detail for several small molecules.

Publications:

Gilson, M.K., McCammon, J.A., and Madura, J.D., **"Molecular Dynamics Simulation with a Continuum Model of the Solvent,"** J. Comput. Chem 16:1081-1095, 1995.

Wlodek, S.T., Antosiewicz, J., McCammon, J.A., Straatsma, T.P., Gilson, M.K., Briggs, J.M., Humblet, C., and Sussman, J.L., **"Binding of Tacrine and 6-Chlorotacrine by Acetylcholinesterase,"** (in press).

Marrone, T.J., Gilson, M.K., and McCammon, J.A., **"Comparison of Continuum and Explicit Models of Solvation: Potentials of Mean Force for Alanine Dipeptide,"** J. Phys. Chem. (in press).

12. *Modeling of Enzyme Mechanisms using Quantum Chemistry*

B.D. Wladkowski, W.J. Stevens, and M. Krauss

Objective: To develop and apply new modeling methods that combine high-resolution protein structure data with state-of-the-art quantum mechanical methods to predict and analyze the microscopic details of enzymatic mechanisms.

Problem: Currently, there is no reliable modeling method that can provide detailed information about enzymatic reaction pathways. Such information can be valuable in many biotechnology applications, such as rational drug design and protein engineering, that are enhanced by knowledge of enzymatic reaction pathways including the structure of transition states and intermediates and the energetic barriers for rate limiting steps. Advances in X-ray crystallography and NMR spectroscopy have resulted in increased availability of high-resolution protein structures, but the structures seldom include information about intermediates in enzymatic reactions. Classical molecular mechanics and molecular dynamics based on experimental structures are incapable of describing the breaking and making of chemical bonds. Only quantum mechanics can provide the needed information.

Approach: Recently developed "effective fragment potential" (EFP) methods may be used to enable quantum mechanical calculations on very large systems, such as protein/substrate complexes. High resolution X-ray or NMR structures can be used to constrain the positions of the protein fragments in the chemically "active" and nearby spectator regions. With these structural constraints, it becomes tractable to carry out high-quality calculations on the chemistry in the active region. The direct chemical roles of specific protein residues can be predicted and analyzed as well as the structures and electrostatic properties of key reaction intermediates. The mathematical methods and computational algorithms required for the EFP method have been incorporated into the widely-distributed GAMESS quantum chemistry software through a cooperative agreement with Iowa State University (Professor Mark Gordon).

Results and Future Plans: The EFP method has been used initially to model the enzymatic reaction of bovine pancreatic Ribonuclease A (RNase), which is one of the most studied enzymes both structurally and enzymatically. RNase catalyzes the hydrolysis of a phospho-ester bond in RNA. There is considerable controversy surrounding the specific role of the active site residues in the mechanism and the structures of key intermediates. Computational results for the first step in the hydrolysis mechanism, transphosphorylation to form a cyclic phosphate intermediate, confirmed that the reaction involves a metastable pentacoordinate phosphorane intermediate. The calculations predict that the first step in the mechanism is protonation of the substrate, which is in agreement with recent, controversial experimental interpretations. The second step is deprotonation of the 2' hydroxyl group of the ribose, allowing the oxygen to attack the phosphorous to form the pentacoordinate intermediate. The remainder of the transphosphorylation reaction has been examined and the roles of nearby residues have been evaluated.

In the next phase of this project, the EFP method will be applied to the enzyme beta-lactamase, whose enzymatic mechanism is less well understood. Beta-lactamase is a bacterial enzyme that hydrolyzes β-lactam antibiotics and is thus responsible for one type of bacterial resistance to drugs. An understanding of the hydrolysis mechanism will aid in the development of new pharmaceuticals. In addition to this new application, the incorporation of the EFP method into the GAMESS computer software will continue to be refined and tested.

Publications:

Wladkowski, B.D., Krauss, M., and Stevens, W.J., "**Ribonuclease A Catalyzed Transphosphorylation: An Ab Initio Theoretical Study,**" J. Phys. Chem. 99, 6273-6276 (1995).

Wladkowski, B.D., Krauss, M., and Stevens, W.J., "**Transphosphorylation Catalyzed by Ribonuclease A: Computational Study using ab initio Effective Fragment Potentials,**" J. Am. Chem. Soc. (in press).

13. *Examining Rhodopsin Folding and Assembly Through Expression of Polypeptide Fragments*

K. D. Ridge, S. S. J. Lee (Univ. of Maryland), and N.G. Abdulaev (Shemyakin and Ovchinnikov Institute of Bioorganic Chemistry, Moscow, Russia)

Objective: To understand the folding of signal-transducing, membrane proteins using rhodopsin as a prototype for the large class of proteins with a seven-trans-membrane helix structure.

Problem: The dim-light photoreceptor rhodopsin is a prototypical member of the superfamily of G-protein coupled receptors sharing the seven-transmembrane-helix structural motif which regulate a variety of sensory, hormonal, and neural responses. Rhodopsin is composed of the apoprotein opsin, a single polypeptide chain of 348 amino acids, and a covalently linked 11-*cis*-retinal chromophore. While the chemical aspects of rhodopsin structure have yielded to investigation, the folding and assembly of the photoreceptor are far from being understood at the molecular level.

Approach: The strategy we have adopted is to provide a detailed analysis of the folding and assembly of rhodopsin by identifying regions of the opsin polypeptide chain which contain sufficient information to fold independently, insert into a membrane, and assemble to form a functional photoreceptor. It is well known from studies on a number of soluble globular proteins that certain polypeptide fragments behave as independent folding domains and that many of these fragments can be functionally recombined. In this study, opsin fragments have been generated by genetic manipulation of the bovine opsin gene and examined for their ability to fold and assemble into a retinal-binding protein after coexpression in mammalian cells.

Results and Future Plans: The present results show that the coexpression of two or three complementary fragments allows the formation of a noncovalently rhodopsin. These findings strongly suggest that the functional assembly of rhodopsin is mediated by the association of multiple protein-folding domains. Additionally, while many of the opsin polypeptide fragments contain sufficient information to fold and insert into a membrane, only those separated at specific locations along the polypeptide chain assemble to form a functional photoreceptor. The localization of additional sites, where discontinuity of the opsin polypeptide chain allows fragment complementation, is being pursued.

Publications:

Ridge, K.D., Lee, S.S.J., and Yao, L.L., "**In vivo Assembly of Rhodopsin from Expressed Polypeptide Fragments,**" Proc. Natl. Acad. Sci. USA 92, 3204-3208 (1995).

Ridge, K.D., Lee, S.S.J., and Abdulaev, N.G., "**Examining Rhodopsin Folding and Assembly Through Expression of Polypeptide Fragments,**" J. Biol. Chem. (in press).

14. *Biological Macromolecule Crystallization Database on the World Wide Web*

J.E. Ladner, M. Tung, and G.L. Gilliland

Objective: To create a version of the NIST/ NASA/CARB Biological Macromolecule Crystallization Database (BMCD) that is directly accessible via the Internet to scientists engaged in X-ray crystallographic studies of biological macromolecules.

Problem: Crystals of biological macromolecules are prerequisites for the determination of three-dimensional structures by X-ray diffraction techniques. The crystal structure of a biological macromolecule is essential for protein engineering, drug design, protein folding and basic research programs that require structural information. The development of crystallization protocols for biological macromolecules is an empirical process that takes advantage of previous successes. The direct access to evaluated data from the literature by scientists engaged in crystallographic studies would facilitate crystal growth activities. In the past, the BMCD has been available only for PC's through the Standard Reference Data Program.

Approach: To provide a broader distribution of the BMCD to the scientific community, network access to the BMCD is required. The porting of the BMCD to a UNIX platform would facilitate this and provide a much more robust environment for expanding the capabilities of the software. The porting will also require reformatting much of the data contained in the BMCD. These data consist of the crystal data and crystallization conditions for biological macromolecules for which crystals suitable for single-crystal X-ray diffraction studies have been produced. The data include summary information on each biological macromolecule that has been crystallized, crystal data, crystallization conditions, and complete references. The BMCD also includes protocols and results of crystallization experiments undertaken in a microgravity environment (space flight). These data are comprised of entries from the NASA Protein Crystal Growth Archive, NASA-sponsored protein crystal growth experiments, and other microgravity crystallization studies sponsored by international organizations.

Results and Future Plans: The BMCD has been successfully ported to a UNIX platform including a complete rewrite of the database software and data conversion. This version of the BMCD provides direct network access, including a sophisticated user interface that allows browsing, searching, downloading and displaying the data. The online version of the BMCD is available through the Internet at the URL address http://ibm4.carb.nist.gov:4400/carb.html. The next phase of development of the BMCD will involve protocols for continually updating the data and developing direct network interactions with other important structural biology databases such as the Protein Data Bank. Future plans also include providing software tools to facilitate the design of experiments to reproduce the crystallization experiments for a particular biological macromolecule. This will be extended to develop initial crystallization screens for modified (or mutant) biological macromolecules and for those that are members of a specific family of biopolymers that have already been the subject of structural investigations. A long range goal is the development of a general strategy for the crystallization of a unique biological macromolecule of a particular class or category.

Publications:

Gilliland, G.L., "**The Biological Macromolecule Crystallization Database,**" Methods in Enzymology (in press).

15. *The Crystal Structure of a Specific Protein 'Foldase': the Prosegment-Subtilisin BPN' Complex*

T. Gallagher, L. Wang (CARB/UMBI), P. Bryan (CARB/UMBI), and G. Gilliland

Objective: To understand the folding of proteins that lack independent folding pathways.

Problem: The pathways by which proteins fold into their native structures, and thereby acquire their catalytic and other functional properties is both a preeminent scientific challenge and a vexing problem for biotechnologists, who often experience problems in getting proteins to fold efficiently.

Approach: Proteins with the apparent function of assisting in the folding of other proteins (Chaperonins) have been identified, and there is a class of proteins that lacks independent folding pathways to the native state. The 275-residue serine protease subtilisin BPN', a detergent enzyme, belongs to the class of proteins that lacks an independent folding pathway. The folding of subtilisin BPN' is dependent on its 77-residue prosegment, which is then autocatalytically removed to give the mature enzyme. Refolding of subtilisin is extremely slow unless catalyzed by the independently expressed prosegment. The prosegment-subtilisin BPN' was isolated, crystallized, and the three-dimensional structure was determined by a novel implementation of molecular replacement method, solvent flattening and phase combination techniques.

Results and Future Plans: A complex of subtilisin BPN' and its independently expressed prosegment was determined at 2.0 Å resolution by X-ray crystallographic techniques. The prosegment forms a compact domain that binds subtilisin BPN' through an extensive interface involving the enzyme's two parallel surface helices. The structure does not immediately explain how the folding catalysis occurs, but provides several intriguing clues. The C-terminus of the prosegment is observed to occupy the enzyme's active site. Therefore, the structure of the complex supports a unimolecular mechanism for prosubtilisin cleavage, involving a 25 Å rearrangement of the N terminus in a late folding step. The structure is being analyzed in the context of ongoing work at CARB in protein folding and protein engineering, providing a basis for site-directed mutagenesis studies that will investigate the catalytic role of the prosegment in forming the three-dimensional structure of the mature subtilisin.

Publications:

Gallagher, T., Gilliland, G.L., Wang, L., and Bryan, P., "**The Prosegment-Subtilisin BPN' Complex: Crystal Structure of a Specific 'Foldase',**" Structure 3, 907 (1995).

16. *Developing a Model for Protein-Carbohydrate Interactions Using Molecular Dynamic Simulations*

J.W. Brown and F.P. Schwarz

Objective: To develop a computational model to predict the energetics of carbohydrate-protein interactions and to identify the specific interactions on the molecular level involved in the binding of carbohydrates to proteins.

Problem: To design drugs which bind more effectively to their targets, it is necessary to develop a model to predict the binding affinities based on the specific intermolecular interactions between the drug and the target protein. The highly specific binding of carbohydrates to proteins would provide an excellent model system for these predictions.

Approach: Molecular dynamics simulations may be used to accurately predict the differences in binding enthalpies of a series of carbohydrates bound to the same protein site. The differences between the average minimum energies of the solvated carbohydrate/protein complexes and the minimum energies of the solvated carbohydrates alone should provide the differences in binding enthalpies. The binding enthalpies can be determined experimentally by titration calorimetry, and the extent of agreement between the computed and experimental differences may be used to ascertain the validity of the computational model.

Results and Future Plans: Molecular dynamics simulations were performed on carbohydrate-protein complexes in which the binding site was immersed in a water shell using the Biosym Discover Software. The methyl-α-D-mannopyranoside (MeMan)-concanavalin crystal structure was obtained from the Brookhaven Protein Data Bank and was used as the basic starting structure for the dynamic simulations. The sugar in this starting structure was modified using computer graphics for use in simulations of the α-D-mannopyranose (Man), α-methyl-D-glucopyranoside (MeGlu), and α-D-glucopyranose (Glu) ligated complexes of concanavalin A. TIP3P model water molecules were used for the solvent. Molecular dynamics simulations were also performed on the carbohydrate with the solvent alone. Molecular dynamics simulations consisting of a short period of equilibration followed by a longer period of simulation yielded differences between the minimum energies of the complexes and the MeM-concanavalin A complex of 8.11 kJ mol^{-1} for Man, 14.7 kJ mol^{-1} for MeGlu, and 9.41 kJ mol^{-1} for Glu which compare favorably in magnitude with the experimental binding enthalpy differences of 5.3 ± 1.2 kJ mol^{-1} for Man, 9.6 ± 1.1 kJ mol^{-1} for MeGlu, and 11.8 ± 1.0 kJ mol^{-1} for Glu. This implies that differences in the energetics of the carbohydrate with water alone are small, which has been confirmed experimentally by the agreement of carbohydrate heats of solution and heats of melting. The minimum energies of the carbohydrates in water are now being computed. The simulations also show the importance of water bridging molecules between the carbohydrate OH groups and the amino acid groups at the binding site, and that hydrophobic groups on the portion of the carbohydrate exposed to the solvent tend to "push" the carbohydrate more tightly into the binding site, increasing the binding enthalpy.

This model will be tested for carbohydrate derivatives where the OH groups have been replaced by F atoms and for other proteins where the structures of their carbohydrates complexes are known to further evaluate the validity of this approach.

Publications:

Schwarz, F.P., Misquith, S., and Surolia, A., "**Thermodynamics of Substituted D-Glucopyranoside Derivatives Binding to Concanavalin A, Pea (Pisum sativum) Lectin, and Lentil (Lens culinaris Lectin),**" Biochem. J. (in press).

17. Hybrid Bilayer Membranes as Biomolecular Materials

A.L. Plant, M.L. Lewis, and D. Vanderah

Objective: The quest to develop sensors, bioelectronics, and other novel materials with unique structural and/or functional properties has led to an intense interest in biomimetic materials. We are characterizing one such material for what can be learned about cell membranes and membrane protein structure and function.

Problem: There are a number of potential commercial applications for a class of biological molecules which naturally reside in cell membranes. Such molecules include light harvesting proteins, transport proteins, cell-membrane receptors, and redox enzymes. In general, these proteins are not fully active, nor stable, outside of their normal lipid membrane environment. Rugged planar membrane-like constructs that allow membrane proteins to be immobilized, organized, and active, need to be developed and characterized. We are developing a planar biomimetic membrane as a research tool for studying the structure and activity of these large and complex proteins. This material may eventually be useful as a component of commercial devices.

Approach: Recent studies have led to the development of a novel approach for preparing a biomimetic material which is analogous to the lipid membranes of cells. This material is composed of two self-assembling monolayers, one which is nonbiological (alkanethiol) and a second which originates from biological cell membranes (phospholipid). This hybrid bilayer membrane (HBM) is formed spontaneously on a planar metal surface, and is unique in that it is biomimetic, yet supported and rugged. It is the first cell membrane-like material which is rugged enough and easy enough to fabricate that it has practical applicability to large-scale use.

Results and Future Plans: Several kinds of studies have been carried out to characterize the HBM. We have used electrochemical techniques to show that it is a highly insulating layer which responds in a physiologically-relevant manner to protein toxins and anesthetics. Using surface-enhanced Raman spectroscopy, we have studied the details of the molecular organization of this material. Vibrational spectroscopic studies are continuing in collaboration with studies in the Materials Science and Engineering Laboratory, using molecular modeling and neutron reflectivity. These studies will provide detailed understanding that will aid the development of improved techniques for membrane protein structure determination. Synthetic approaches to modification of the HBM are being developed that will allow incorporation of transmembrane proteins. In addition, the HBM is the focus of a CRADA with SmithKline Beecham Pharmaceuticals. The goal of the CRADA is to use the HBM as a planar membrane matrix in which to incorporate cell surface receptors for identification and characterization of synthetic and natural pharmacological agents. The HBM permits the measurement of the kinetics of binding of membrane receptors with their ligands. It will also be useful for studying the dynamic events that occur at cell membrane surfaces due to multivalent interactions between receptors and ligands. Preliminary studies of dynamic light scattering from an evanescent wave suggest that this method will allow us to use HBMs as part of a model system to understand the mechanism of the movement of cells at tissue surfaces.

Publications:

Plant, A.L., Guegetchkeri, M., and Yap, W., **"Supported Phospholipid/Alkanethiol Biomimetic Membranes: Insulating Properties,"** Biophys. J. 67, 1126-1133 (1994).

Plant, A.L., Brigham-Burke, and O'Shannessy, **"Phospholipid/Alkanethiol Bilayers for Cell Surface Receptor Studies by Surface Plasmon Resonance,"** Anal. Biochem. 226, 342-348 (1995).

Gaigalas, A.K., Hubbard, J.B., Plant, A.L., and Reipa, V., **"Application of Evanescent wave Scattering to the Study of the Motion of Liposomes Near an Interface,"** J. Coll. Interface Sci. 175, 181-189 (1995).

18. *Membrane Pore-Forming Proteins as Novel Engineered Sensors*

J. Kasianowicz and B. Robertson

Objective: We are designing and characterizing genetically engineered mutants of a pore-forming protein to determine its secondary structure and to develop nanoscale sensors for a variety of water soluble ligands.

Problem: The difficulty of crystallizing membrane-bound proteins has hindered the elucidation of their structure and function. Thus, new methods for determining protein structure are needed. Some methods have the potential to aid the rational design of proteins that can be used in biosensor applications.

Approach: We are adapting proteins that self-assemble to form well-defined nanoscale pores in lipid bilayers for detecting, with high specificity, a variety of polymers, chemical compounds, ions, and toxins in water. Protein composition is being modified to enhance pore-transport detectability and selectivity. The method of detecting a ligand is simple: the reversible binding of a ligand to a target site in front of or inside the pore will block ionic current through the pore. Analysis of the mean and fluctuating ionic current determines the ligand concentration and reaction dynamics. We are also using this technique to determine the secondary structure of the pore formed by α-toxin by placing a novel ionizable residue, which acts as one coordination site for a divalent cation, into the protein's primary structure. A second ionizable site is introduced either two, three or four residues downstream, and the sensitivity of these mutants to divalent cation-induced blockage is measured. Heavy metals interact with coordination sites only if both residues are in the pore and in close proximity. If the ligand binds to sites that are spaced two or four residues apart, the pore's structure must be β-sheet. However, if the binding site is accessible to ligand when the residues are three to four residues apart, the pore is formed by an α-helix.

Results and Future Plans: We've demonstrated that protons binding to the α-hemolysin channel can alter its conducting properties and that the dynamics of the ionization reactions could be determined using spectral analysis of the proton-induced current fluctuations. We determined a region in the primary structure that lines the pore and found that a simple mutation could confer divalent cation sensitivity to the channel. This was accomplished by replacing 5 consecutive residues near the midpoint of the polypeptide with histidine residues, since the imidazole rings of spatially adjacent histidines can coordinate metal cations. Recently, we found that the pore has a β-sheet motif in that region and that the selectivity for different divalent cations is moderate. Future efforts will be directed towards designing and characterizing pores with high specificity and sensitivity that function in membranes rugged enough for biosensor applications.

Publications:

Walker, B., Kasianowicz, J.J., Krishnasastry, M., and H. Bayley, **"A Pore-forming Protein with a Metal Actuated Switch,"** Protein Engineering 7, 655-662 (1994).

Kasianowicz, J., Walker, B., Krishnasastry, M., and H. Bayley, "**Genetically Engineered Pores as Metal Ion Biosensors,**" MRS Symp. 330, 217-223 (1994).

Kasianowicz, J.J. and Bezrukov, S.M., **"Protonation Dynamics of the α-toxin Ion Channel from Spectral Analysis of pH Dependent Current Fluctuations,"** Biophysical J. 69, 94-105 (1995).

19. Optical Stimulation and Proton Pumping by Bacteriorhodopsin

H. Weetall, B. Robertson (NIST), T. Dyukova, A. Drushka (Institute of Theoretical and Experimental Biophysics, Moscow, Russia), and M. Ostrovsky (Russian Academy of Sciences)

Objective: To understand the mechanism of proton pumping within the transmembrane protein, bacteriorhodopsin, and to modify the spectral properties and kinetics while maintaining opto-electronic activity in the form of proton pumping.

Problem: Bacteriorhodopsin has a photocycle that involves several photo-intermediates. This photocycle is dependent on the amino acid sequence of the protein and the structure of the chromophore, retinal, within the protein. Modification of any of several important amino acids or modification of the retinal causes major changes in the kinetics and photocycle spectrum. The use of this protein in technological development including molecular electronic applications requires an understanding of these characteristics and ability to modify these specific properties.

Approach: Wild-type and mutant versions of bacteriorhodopsin are available or can be obtained through genetic modification. Retinal analogs have been shown to have a major effect on spectral and opto-electronic properties of the wild-type protein. We are systematically examining the effect of specifically-designed retinal analogs in proton-pumping and spectral properties, both wild-type and mutant bacteriorhodopsins. These experiments will lead to a model that will allow us to predict the affect that either amino acid substitution or retinal substitution will have on the kinetics and spectral properties of the protein. In addition we expect to learn which amino acids and which retinal analog structures permit the photocycle to be retained and therefore proton pumping to continue.

Results and Future Plans: We have examined the kinetics, spectral properties, and opto-electronic proton-pumping capabilities of films and suspensions of several mutants and analogs of both the wild-type and mutant bacteriorhodopsins, including the D96N mutant in which aspartate at position 96 is replaced by asparagine. Substitution of the retinal in both the wild-type and the D96N mutant with the 4-keto-retinal caused a blue shift in the spectrum and a major decrease in the decay time from the M-state to ground state of the order of 60-90 minutes. The proton pumping capabilities of both 4-keto analogs was decreased by approximately 50%.

These results suggest that major changes in the spectrum and kinetics of bacteriorhodopsin are caused not by changes in the amino acid sequence but by modification of the retinal. It is true that some of the mutants no longer show a photocycle. However, those that do may show relatively small kinetic and spectral changes. Substitution of the chromophore in the molecule appears to have major effects.

In FY96 we plan to examine the effect of the azulene series and fluorine-substituted retinals. We believe that these analogs will give us enough information to initiate development of a useful model for the mechanism of action of this transmembrane protein.

Publications:

Cullin, D.W., Vsevolodov, N.N, and Dyukova, T.V., **"Holographic Properties of Triton X-100 treated Bacteriorhodopsin Embedded in Gelatin Films,"** BioSystems 35, 141-144 (1995).

Cullin, D.W., Vsevolodov, N.N., Dyukova, T.V., and Weetall, H.H., **"Optical Properties of Triton X-100 treated Purple Membranes Embedded in Gelatin Films,"** Supramolecular Science 2. 25-32 (1995).

Lukashev, E.P. and Robertson, B., **"Bacteriorhodopsin Retains its Light-induced Proto-pumping Function After being Heated to 140° protein.C."** Bioelectrochem. Bioenergetics 37, 157-160 (1995).

Robertson, B. and Lukashev, E.P., **"Rapid pH change Due to Bacteriorhodopsin Measurement with a Tin-oxide Electrode,"** Biophys. J. 68, 1507-1517 (1995).

Weetall, H.H., **"D96N Mutant Bacteriorhodopsin Immobilized in Sol-Gel Glass,"** Appl. Biochem. Biotechnol. 49, 241 (1994).

20. 1995 Activities of the Consortium on Advanced Biosensors

***H. Weetall**, D. Vanderah, R. Ashton, and V. Silin (Institute of Biochemistry, Vilnius, Lithuania)*

Objective: To understand the mechanisms involved in non-specific binding (NSB) of proteins to surfaces and to find methods of preventing it.

Problem: Non-specific binding of proteins to surfaces is a significant problem in biosensor development. The reduction of non-specific adsorption can significantly increase the sensitivity and selectivity of biosensors by decreasing the noise level caused by the non-specifically bound proteins.

Approach: In order to prepare chemically defined surfaces for protein adsorption measurements, we have chosen to modify gold surfaces with alkane thiols. The terminus of the alkane chain can be modified by the addition of desired functional groups, and because the alkane thiols are self-assembling, they form a well covered surface. We chose to examine the binding of bovine serum albumin (BSA) and human immunoglobulin (hIgG) to surfaces terminating in different functional groups. The groups chosen for study included: CH_3, COOH, OH, phenol, NH_2, a sugar, and ethylene oxide. The methods chosen for studying this problem included: radio labeling, ellipsometry, and surface plasmon resonance techniques

Results and Future Plans: The results indicate that irreversible NSB occurs for both proteins on the surface terminated with CH_3. NSB occurs to a lesser extent with most of the other surfaces. In each of these cases, the protein could not be totally removed by washing. However, in the case of the ethylene oxide surface, no detectable binding was observed even when very high concentrations of proteins were applied.

Long exposure of the ethylene oxide terminated surface to whole serum caused binding of what appears to be lipoproteins. Once these proteins are bound, BSA and hIgG could be detected using immunoassay techniques.

In FY96 we plan to continue to examine the binding of the putative lipoprotein fraction to the ethylene oxide surface. We will attempt to identify this material that seems to exchange with the loosely bound proteins adsorbed in the presence of whole serum.

21. Applied Biosensor Research

J.J. Horvath, S. Glazier, H.H. Weetall, M. Gueguetchkeri, E. Campbell (The Nitrate Elimination Co., Lake Linden, Michigan), and W. Campbell (The Nitrate Elimination Co., Lake Linden, Michigan)

Objective: To explore different methods of biosensor construction that may lead to devices which have immediate, real-world applications.

Problem: Despite the great volume of research, and the great number of potential applications for biosensors, there are still few areas in which biosensors are routinely used as analytical tools. Environmental monitoring is a particularly important application for biosensors. We have targeted aromatic pollutants, nitrate ion, and nitric oxide for biosensor development.

Approach: Fluorescence polarization is being used to quantify aromatic pollutants which compete with fluorescent dyes for DNA binding sites. This work is being carried out with partial support from the Environmental Protection Agency. Through a CRADA with The Nitrate Elimination Co., enzyme-based electrodes are being developed for potential use in testing drinking water for nitrates, which enter water supplies through agricultural runoff and industrial emissions. The oxygen binding protein, hemoglobin, is a component in a novel optical sensor to quantitate nitric oxide, a metabolic product as well as an environmental reaction intermediate.

Results and Future Plans: A large number of aromatic pollutants have been detected via DNA intercalation at concentrations near those found for such compounds in environmental samples. Real mixed matrix samples have been successfully tested by this method. In an effort to improve sensitivity, different sources of DNA were studied to test the possibility that intercalation is affected by nucleotide composition; no base specificity was

detected. Future work will include continued efforts to develop fiber-optic sensors for field use.

Using highly stable nitrate reductase enzyme preparations, electrodes have been constructed which will respond to nitrate ion at levels near or below the EPA limit for nitrate in drinking water (10 ppm). We are currently examining a number of different electron transfer mediators to improve the selectivity and range of the response, and to improve the useful lifetime of the enzyme electrode system.

The optical sensor for nitric oxide uses hemoglobin as the active sensing element. When hemoglobin binds NO, its optical absorbance changes in a manner analogous to its binding of oxygen. The sensor was tested for its sensitivity to detect nitric oxide produced by cultured mouse macrophage cells. While the response was sensitive to NO concentration, the sensor required an oxygen-free atmosphere, and so was difficult to use.

Publications:

Horvath, J.J., Gueguetchkeri, M., Gupta A., Penumatchu, D., and Weetall, H.H., "*A* **New Method for the Detection and Measurement of Polyaromatic Carcinogens and Related Compounds by DNA Intercalation,"** ACS Symposium Series (in press).

II. Chemical Kinetics and Thermodynamics Division (833)

Sharon G. Lias, Chief

A. Division Overview

The Chemical Kinetics and Thermodynamics Division is the nation's reference laboratory and the primary resource within the Chemical Science and Technology Laboratory for expertise and information on the rates, mechanisms, and energetics of chemical change at the molecular level. In order to provide the quantitative information on chemical stability needed by the Division's industrial, academic, and governmental customers, the Division maintains state-of-the-art facilities for making calorimetric and kinetic measurements, generates theoretical studies and calculations, develops measurement techniques and methodologies, certifies Standard Reference Materials (SRMs), and generates databases of evaluated numeric data.

Both chemical thermodynamics and chemical kinetics deal with aspects of chemical stability. Chemical thermodynamics is concerned with the energetics of chemical transformations; this kind of information is necessary in order to determine the feasibility or spontaneity of a given process, and permits a prediction of the equilibrium yields of reacting chemicals. Chemical kinetics is the study of the rates of chemical reactions, the factors which influence those rates, and the detailed mechanisms of the reactions. The prediction or control of a process involving chemical change is only possible when one has a good understanding of the kinetics and thermodynamics of the process. A detailed understanding of the energetics and mechanisms of chemical change is at the very heart of chemistry, and constitutes an important goal of science.

Because data on the chemical thermodynamics and kinetics of compounds and processes are necessary for understanding and modeling any system where chemical change is important, it follows that societal applications of - and needs for - such data are numerous and diverse. A few examples of technical subject areas where such data are required are: combustion processes, effects of pollutants on the earth's atmosphere, industrial chemical processing, biological and medical processes, and synthesis of materials.

In 1995, the work of the Division was carried out by 49 chemists and 5 supporting personnel (28 NIST employees, 22 full-time Guest Researchers, one on-site contractor, and three on-site Cooperative Research Grantees), who have expertise in gas and liquid phase kinetics, thermodynamics, optical and mass spectroscopy, and computational chemistry. Administratively, the Division's work is carried out in three Groups: the Experimental Chemical Kinetics Group, the Kinetics Data Centers Group, and the Chemical Thermodynamics Group. Reflecting the emphasis on the production of chemical databases, there are four specialized Data Centers and one data project within the Division: Chemical Thermodynamics, Chemical Kinetics, Ion Kinetics and Energetics, Mass Spectrometry, and the Structures and Properties Project.

Current Division programs treat **Thermodynamics Reference Measurements** and **Kinetic Reference Measurements**, as well as **Atmospheric Kinetics**. Other programs focus on the Division's primary dissemination mechanism for reaching the nation's technical communities, namely the production of expert chemical reference databases: **Chemical Standard Reference Data Evaluation**, and **Database Delivery Mechanisms**.

The **Thermodynamics Reference Measurements Program** is comprised of projects carried out in the Division's four calorimetry laboratories. The standard molar enthalpy of formation of a compound is a fundamental thermodynamic property needed for an understanding of the molecular energetics and feasibility of the chemical reactions of any given substance; the Division's precision oxygen and fluorine bomb calorimetry laboratories provide measurements of enthalpies of formation of pure compounds. The

fluorine bomb calorimetry facility, which allows determinations of the thermochemical properties of compounds that can not be burned in oxygen, is unique in the world. The oxygen-bomb facility is also unique in that determinations can be made with very small amounts of sample (10-15 milligrams), permitting work on compounds not available in larger quantities. The measurements of standard molar enthalpies of formation can be combined with data generated by the low temperature heat capacity calorimeter to permit a prediction of chemical equilibrium constants for systems of interest.

Activities in these three laboratories focus on the generation of thermochemical data of importance to industry. For example, an industrial consortium - the Design Institute for Physical Property Data (DIPPR) - has identified a number of industrially-important compounds for which thermochemical data are lacking. Because of the compatibility between the goals of DIPPR and those of the Thermodynamics Reference Measurements Program, experimental work on a set of these compounds was initiated a year ago, and measurements on the first targeted compounds were completed in 1995.

We are developing additional calorimetry measurement capability using flow and differential scanning calorimetries to determine the thermochemical properties of aqueous solutions at temperatures below the freezing point of water. There have been few experimental determinations of such information, although the data are important for applications ranging from the operation of equipment in cold environments to understanding the heterogeneous chemistry occurring on the surfaces of ice crystals in the upper atmosphere.

The **Kinetic Reference Measurements Program** includes projects on condensed phase kinetics, high temperature gas phase kinetics, and work now being initiated on the characterization of plasma chemistry. The new effort on plasma chemistry is an outgrowth of a still active long-term project on the development of advanced diagnostic tools for making kinetic measurements. During the year, progress was made on the construction of a standard plasma reactor, the second-generation Gaseous Electronic Conference (GEC) Reference Cell, to be used in the project; the facility is designed to be used with various laser-based diagnostics such as degenerate four-wave mixing, laser-induced fluorescence, or cavity ring-down spectroscopies.

Much of the condensed phase kinetics work is focussed on the development of solar energy storage technology - a green technology in the literal sense of the word since the research involves finding substitutes for chlorophyll (which is unstable when removed from the plant matrix and can not be used in industrial environments) to absorb energy from the sun and photogenerate hydrogen and oxygen from water. Compounds called metalloporphyrins, which are chemically related to both chlorophyll and hemoglobin, are explored for use as efficient photosensitizers for solar energy conversion and storage in the project, which is sponsored by the Department of Energy.

The **Atmospheric Kinetics Program** addresses measurement needs for hte determination of gas phase kinetic parameters with specific attention to the impact of man-made chemicals on the planetary atmosphere. Begun in the early 1970's, this NIST effort has substantially contributed to the understanding of reactions occuring in the earth's ozone layer. Division members hold important leadership positions in relevant national and international organizations, such as NASA's Upper Atmosphere Research Program, and the Scientific Steering Committee of the International Network for the Detection of Stratospheric Change. Two Division members are members of the NASA Panel for Data Evaluation, the panel which provides the definitive recommendations of data for modeling stratospheric chemistry.

The experimental program of the Division's atmospheric kinetics laboratory involves the measurement of the gas phase kinetic parameters for chemical reactions important in atmospheric chemistry, with emphasis on processes which relate to the fate of natural and man-made trace gases in the troposphere, their chemical role in the stratosphere, and problems surrounding the depletion of stratospheric ozone. Other experiments involve determinations of the absorption cross sections of relevant molecules in the upper troposphere and lower stratosphere; such information is needed to predict the atmopheric

lifetimes of particular compounds. Because of the low absorption cross sections of many molecules of interest, reported measurements have often been strongly in error because of the effects of scattered light; techniques developed in the Division permit the accurate determination of very small absorption cross sections.

The most important mechanism for disseminating Division outputs to the technical community is the generation of technical databases. This work is carried out under two Division programs, **Chemical Standard Reference Data Evaluation** and **Database Delivery Mechanisms**, which are loosely tied together. The first, the **Chemical Standard Data Evaluation Program**, includes those activities involving collection and assessment of the validity of numeric technical data taken from the chemical literature. The **Database Delivery Mechanisms Program**, as the name implies, is concerned with the development of software and user interfaces for use with NIST chemical databases on personal computers and on the internet. This program also includes the maintenance and improvement of certain analytical chemistry databases; most of the data in such databases is not derived from the chemical literature, and its collection and evaluation involves different procedures from those involved in the development of thermodynamic and kinetic databases.

As mentioned earlier, the work of these two programs is carried out in four Division Data Centers: Chemical Thermodynamics, Chemical Kinetics, Ion Kinetics and Energetics, and Mass Spectrometry. The tie between the experimental programs and the work of the Data Centers is strong, with many Division scientists actively engaged in both experimental and data evaluation projects. The considerable breadth of ongoing experimental activities in the Division ensures that the expertise and insight needed for reliable data evaluation is available. Calculational chemistry expertise available in the Division supports both experimental and data evaluation work, but has as its primary focus the evaluation of chemical data.

The names of the major database development/ maintenance projects in the Division parallel the names of the Data Centers/Projects. These are: the New NIST/JANAF Thermochemical Tables (Chemical Thermodynamics Data Center); the Chemical Kinetics Database and the Solution Kinetics Database (Chemical Kinetics Data Center); the Positive Ion Energetics, Negative Ion Energetics, and the Proton Affinity Databases (Ion Kinetics and Energetics); the NIST/EPA/NIH Mass Spectral Database and the NIST/EPA Vapor Phase Infrared Database (Mass Spectrometry Data Center); Structures & Properties Database and Program (Structures & Properties Project).

In 1995, all on-going evaluation efforts in the Chemical Thermodynamics Data Center and all earlier thermodynamics data evaluation projects were pulled together into a single, focussed project aimed at the production of an update of the well-known JANAF Thermochemical Tables, which is intended to replace both the JANAF Thermochemical Tables and the outdated "NBS Tables of Chemical Thermodynamic Properties." A critical mass of evaluation personnel was achieved by supplementing Data Center staff with additional expert evaluators who came to NIST as Guest Researchers to collaborate on the project. Dr. Malcolm Chase of the Standard Reference Data Program, who is the Editor of the original JANAF Tables, spent full time in 1995 on this project. Although significant progress toward the long-term goal was made during the year, the future of the project is currently under a cloud because of an unexpected loss of funding from SRD.

The project in the Division which probably has the widest visibility outside of NIST is the maintenance and improvement of the NIST/EPA/NIH Mass Spectral Database, a large database of electron mass spectral information which is in use in thousands of analytical chemistry laboratories throughout the world. The collection of spectra is distributed on disk to the public as a searchable database for personal computers, and also in a tape format. All the major manufacturers of mass spectral instrumentation are distributors of the tape version, which is made available to the public as an integral part of the data systems of commercial mass spectrometers. Work on this database, which originated several years ago at the EPA and was transferred to NIST in 1988, has become one of the Division's most vigorous projects, and has led to

numerous spin-off activities. For example, software originally developed for the mass spectral database has been adapted for use with infrared spectra and for structural and sub-structural searching. Based on this code, two new database products - the NIST Vapor Phase Infrared Database and the Structures & Properties Database and Program (which predicts properties of molecules based on user-generated structural drawings) were developed. In 1995, the evaluation of all mass spectra in the entire database collection - an effort which has been on-going for several years - neared completion, and a Windows version of the database was released for use on personal computers.

B. Selected Technical Reports

1. *The New NIST/JANAF Thermochemical Tables*

E.S. Domalski, D.B. Neumann, P.A.G. O'Hare, A. Zywocinski (Polish Academy of Sciences, Poland) and O.V. Dorofeeva (Moscow State Univ., Russia) in collaboration with M.W. Chase (SRD)

Objective: The Chemical Thermodynamics Data Center evaluates thermochemical data needed on compounds that are critical to industry and U.S. technical communities. An immediate objective in 1995 was the production of an update of the JANAF Tables, to be called the NIST/JANAF Thermochemical Tables, which in the future will become the definitive thermochemical database distributed by NIST, the new NIST Thermochemical Tables. These will eventually replace both the JANAF Thermochemical Tables and the old "NBS Tables of Chemical Thermodynamic Properties."

Problem: In 1995, it was evident that there was a real need to update the widely-used JANAF Thermochemical Tables, which are out-of-date, and to bring a new focus to the Division's long-term thermodynamic data-evaluation activities, so a new NIST Thermochemical Data Evaluation project was initiated under the sponsorship of the Standard Reference Data Program. The Chemical Thermodynamics Data Center's focus for this project is on providing evaluated thermochemical data for two important research areas: industrial process applications and environmental modeling. Thermochemical tables for inorganic chalcogenides (sulfides, selenides, and tellurides) play an ever-increasing role in diverse industrial applications such as: electronic component manufacture, petrochemical catalysis, and ferrous/nonferrous alloy production. Chemical and economic optimization of numerous processes benefit from the availability of critically evaluated thermodynamic properties for high temperature needs in vapor phase deposition, extractive metallurgy, and metal sputtering processes. The other initial focus topic, upper atmosphere chemistry, derives its current importance from the on-going attempts to understand the depletion of the earth's ozone layer by man-made chemicals.

Approach: Each thermochemical table to be generated requires a critical assessment of available data, documentation of pertinent references, and selection of best values for specific thermodynamic properties as a function of temperature.

Results and Future Plans: In 1995, all on-going evaluation efforts in the Chemical Thermodynamics Data Center were pulled together into a single, focussed project, and all earlier thermodynamics data evaluation work, as well as the 1994 project on evaluation of thermochemical data on chalcogenide compounds, were incorporated into a new NIST Thermochemical Data Evaluation project. Work is carried out in collaboration with Malcolm Chase of the Standard Reference Data Program, the Editor of the original JANAF Tables, who spent all of 1995 working on the new NIST Thermochemical Data Evaluation project. In addition to the publications listed below, two publications presenting tables with data on inorganic chalcogenides of interest to the semiconductor industry (16 substances) and organic compounds of interest to kinetic modelers (20 compounds) are in preparation. Plans for the future focus on the development of NIST/JANAF Thermochemical Tables for compounds containing the elements N, O, and I, halogenated methanes and radicals, interhalogens, and both inorganic (HCl, HBr, HI, $HClO_4$, HNO_3) and organic acids (HCOOH, CH_3COOH). Also planned are improvements to computer programs for calculating various molecular parameters (force constants, hindered rotations, torsional vibrational modes, etc.).

Publications:

Neumann, D.B., **"NIST-JANAF Thermochemical Tables, 1994 Supplement,"** J. Phys. Chem. Ref. Data 25, Issue Number 2 (in press).

2. *Critical Evaluation of Chemical Kinetics Standard Reference Data*

W.G. Mallard, R.F. Hampson, W. Tsang, V.I. Babushok (Russian Academy of Sciences, Russia), and J.T. Herron (Guest Researcher)

Objective: The Kinetics Data Center evaluates data on the rates of chemical reactions that are needed for modeling natural and industrial processes.

Problem: The Kinetics Data Center originated as a response to the 1971 concerns about the effects of NO_x compounds from supersonic transports on the stratosphere. Current activities of the Data Center include (1) the evaluation of kinetic data needed for use in modeling the chemistry of the upper atmosphere, particularly reactions relevant to the depletion of the earth's ozone layer by man-made chemicals; and (2) the development of a complete database of self-consistent, evaluated kinetic data for use in the modeling of hydrocarbon combustion. The Data Center is officially responsible for evaluations of data on halogenated compounds used by the NASA Panel for Data Evaluation, which is the body officially designated to provide the definitive evaluated data used in modeling chemical processes in the upper atmosphere. R. F. Hampson is a member of the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry.

Approach: The technical literature is routinely scanned and all publications presenting data on the rates of chemical reactions are retrieved, and data relevant to on-going evaluation projects are abstracted for use by the evaluators.

Results and Future Plans: During the past year, Dr. Robert Hampson and Division member Dr. M. J. Kurylo contributed to an expanded and updated NASA-sponsored evaluation of data relevant to stratospheric modeling. Drs. Hampson and Kurylo were responsible for the data sheets covering atmospheric reactions of halogenated species and of SO_x compounds. Dr. John Herron organized and hosted a workshop on "Data Needs for Modeling Aqueous Chemical Kinetics for the Global Atmosphere."

In close collaboration with the Division experimental project on high temperature kinetic studies of incineration systems (described below), work is on-going to use modeling to develop an understanding the physico-chemical basis for the action of fire retardants. A related calculational project carried out in collaboration with members of the Process Measurements Division resulted in the publication of a NIST Technical Note entitled "Thermochemical and Chemical Kinetic Data for Fluorinated Hydrocarbons." Another such project, involving a collaboration between W. Tsang and M. Zachariah (Division 836) developed new insights into the best methods of analyzing high temperature chemically-activated reactions; these insights will permit more accurate evaluations of these pressure-dependent rate constants.

Publications:

Atkinson, R., Baulch, D.L., Cox, R.A., Hampson, Jr., R.F., Kerr, J.A., Rossi, M., and Troe, J., **"Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry. Supplement V. IUPAC Subcommittee on Gas Kinetic Data Evaluation,"** J. Phys. Chem. Ref. Data (in press).

Babushok, V.I., Burgess, D.R.F., Linteris, G., Tsang, W., and Miziolek, A., **"Modeling of Hydrogen Fluoride Formation From Flame Suppressants During Combustion,"** Proceedings of the Halon Alternatives Technical Conference, Albuquerque, New Mexico (in press).

Babushok, V.I., Burgess, D.R.F., Tsang, W., and Miziolek, A., **"Simulation Studies of the Effects of Flame Retardants on Combustion Processes in a Plug Reactor,"** in Halon Replacements: Technology and Science (Miziolek, A. and Tsang, W., Eds.), American Chemical Society Symposium Series, American Chemical Society, Washington, DC, 1995 (in press).

Bedanov, V., Tsang, W., and Zachariah, M.R., **"Master Equation Analysis of Thermal Reactions: Reversible Isomerization and Decomposition,"** J. Phys. Chem. 99, 11452 (1995).

Burgess, D.R.F., Zachariah, M.R., Tsang, W., and Westmoreland, P.R., **"Thermochemical and Chemical Kinetic Data for Fluorinated Hydrocarbons in Flames,"** NIST-TN 1412, Prog. Energy Combustion Sci. (in press).

Burgess, D.R.F., Zachariah, M.R., Tsang, W., and Westmoreland, P.R., **"Key Species and Important Reactions in Fluorinated Hydrocarbon Flame Chemistry,"** in Halon Replacements, Technology and Science (A. Miziolek, and W. Tsang, Eds.), American Chemical Society Symposium Series, American Chemical Society, Washington, DC, 1995 (in press).

Slayden, S.W., Liebman, J.F., and Mallard, W.G., **"Thermochemistry of Halogenated Organic Compounds,"** The Chemistry of Halides, Pseudo-halides and Azides, Vol 2 Supplement D, S. Patai and Z. Rappoport, Eds., John Wiley & Sons, Chichester, England, 361 (1995).

Tsang, W., **"Heats of Formation of Organic Free Radicals by Kinetic Methods,"** in Energetics and Reactivity of Free Radicals (J. Liebman and A. Greenberg,Eds.), VCH Publishers (in press).

3. The Chemical Kinetics and Solution Kinetics Databases

W.G. Mallard, R.D. Levin, D. Frizzell, P. Christian, and J. Reed

Objective: To make evaluated/unevaluated data on the rate constants of chemical reactions available to the technical public. Data on gas phase and condensed phase reactions are presented in the NIST Chemical Kinetics Database and the NIST/NDRL Solution Kinetics Database (which is produced in collaboration with the Notre Dame Radiation Laboratory.)

Problem: The single most important dissemination mechanism for Data Center collections and evaluations is the production of personal computer databases. These databases are provided with software developed in the Data Center, and distributed by the Standard Reference Data Program. The Chemical Kinetics Database first appeared in 1989, and has been updated annually every year since then; there are more than 700 copies in use. The Solution Kinetics Database dates from 1993.

Approach: The technical literature is routinely scanned and all publications presenting data on the rates of chemical reactions are retrieved, and data are abstracted and entered into the database. Software for retrieving and manipulating the data is developed in-house.

Results and Future Plans: Version 6.0 of the Chemical Kinetics Database, containing data relating to over 8800 reactant pairs, was released in FY95. Production of a Windows version of the basic chemical kinetics software and entry system is progressing, and a preliminary version will be available early in FY1996. Work on Version 3.0 of the Solution Kinetics database continued, in collaboration with Notre Dame Radiation Laboratory (NDRL); Division members R. E. Huie and P. Neta have completed a compilation of rate constants for reactions of carbon-centered radicals in solution for addition to this database. Major changes in searching modes were made in Version 2, and therefore only minor new features will be added to this version. Additional changes in

software functionality will probably be delayed until the Windows version is completed. A database of structures of molecules for which data is contained in the Chemical Kinetics and Solution Kinetics Databases is being developed.

Publications:

Mallard, W.G., Westley, F., Herron, J.T., and Hampson, R.F., **"NIST Chemical Kinetics Database, Version 6.0,"** NIST NSRDS Database 17.

4. Updates of the Proton Affinity and the Ion Energetics Databases

***E.P. Hunter**, S.G. Lias, and P.J. Christian*

Objective: The Ion Kinetics and Energetics Data Center produces collections and evaluations of data concerned with the kinetics and thermochemistry of ions in the gas phase.

Problem: In order to understand and model environments where ionization occurs such as mass spectrometry, plasmas, the ionosphere, systems under high energy irradiation, etc., it is necessary to have access to information on the kinetics and thermochemistry of gas phase ions.

Approach: The Data Center maintains collections of data on ionization energies of molecules, appearance energies of fragment ions, proton- and electron-affinities (data file maintained by J. Bartmess at the University of Tennessee), and the thermochemistry of ionic clusters (data file maintained by M. Mautner, Christ Church, New Zealand), and produces publications presenting these data. The data are also disseminated in a personal computer version utilizing the Structures & Properties Software, which was developed in-house and is described below.

Results and Future Plans: The data evaluation project devoted to updating the 1984 Data Center Journal of Physical and Chemical Reference Data publication on proton affinities of molecules was completed this year, and a manuscript and database are being prepared. Edward Hunter's exhaustive evaluation of the proton affinities of 1300 compounds involved extensive interactions with scientists around the world, most notably with computational chemists who have taken an interest in calculating the energetics and entropy changes associated with protonation of neutral molecules. The earlier publication received more citations than any other chemistry paper written in 1984, and there have been numerous requests from the technical public for an update.

During FY95, work on the preparation of the next update of the database of ionization energies and appearance energies neared completion. With the

addition of all data from the early pre-computer publication "Energetics of Gaseous Ions" (Journal of Physical and Chemical Reference Data **6**, Suppl. 1 (1977)) into a computer file, and preparation of a file of structural drawings of all compounds in that file, the update will for the first time include all data going back to the beginnings of such measurements. New data which has appeared since the 1992 cut-off for data inclusion in the current version are also being added for the update.

Publications:

Hunter, E.P., ***"A Brief Overview of the 1995 Proton Affinity Scale,"*** Proceedings of the NATO Advanced Study Institute on Fundamentals and Applications of Gas Phase Ion Chemistry (in press).

5. *Calculational Chemistry Activities*

***K. Irikura**, R.D. Johnson III, and P. Hassanzadeh (George Washington Univ.)*

Objective: To generate and evaluate chemical kinetics and thermodynamics data using computational chemistry, and to develop and evaluate *ab initio* methods for the prediction of molecular energetics and partition functions.

Problem: Accurate thermodynamics and kinetics data are required for successful modeling of atmospheric chemistry, semiconductor processing, industrial chemistry, and many other processes of great economic importance. Unfortunately, the necessary data are often missing or of unknown reliability, destroying the credibility of the affected models. Moreover, data needs often overwhelm available experimental resources. NIST is endeavoring to meet this data requirement.

Approach: *Ab initio* methods of quantum chemistry are sufficiently mature to provide acceptable data for large classes of molecules. In many cases, experimental data for related species can be exploited to produce very reliable, precise predictions. The project is focused on thermochemistry and kinetics, for which the relevant quantities are molecular energetics (enthalpies) and molecular vibrational energy levels (entropies and heat capacities). Available methods are used to produce and evaluate data for specific molecules, and also contribute to the current art through methods evaluation and development.

Results and Future Plans: Most of the effort is directed toward molecules that present unusual experimental difficulties, such as reactive transients or compounds of high toxicity. In the past year, completed work includes calculational studies of: the thermochemistry of disulfur decafluoride (toxicity problem for the electrical industry); the vibrational spectrum of the fluorine monoxide radical (atmospheric chemistry); the thermochemistry of phosphorus fluoride radicals and ions (plasma processing); the thermochemistry of carbonyl fluorides (atmospheric chemistry); the vibrational spectrum of silicon fluoride ions (plasma processing); and evaluation of several methods for

predicting vibrational anharmonicities (contribution to current art). Current and future work includes more studies such as those listed, and also prediction of Benson-type group values, methods development for molecular energetics, and computation of reaction rates. Collaborations, including several within NIST and a few at Dow Chemical, have been very helpful and their importance will increase as work progresses.

Publications:

Buckley, T.J., Johnson, R.D. III, Huie, R.E., Zhang, Z., Kuo, S.C., and Klemm, R.B., **"Ionization Energies, Appearance Energies, and Thermochemistry of CF_2O and FCO,"** J. Phys. Chem. 99, 4879 (1995).

Forney, D., Jacox, M.E., and Irikura, K.K., **"Matrix Isolation Study of the Interaction of Excited Neon Atoms with CF_4. Infrared Spectra of CF_3^+ and CF_3^-,"** J. Chem. Phys. 101, 8290 (1994).

Irikura, K.K., **"Structure and Thermochemistry of Sulfur Fluorides SF_n(n=1-5) and Their Ions SF_n+ (n=1-5),"** J. Chem. Phys. 102, 5357 (1995).

Irikura, K.K., **"Thermochemistry of Disulfur Decafluoride, S_2F_{10},"** J. Chem. Phys. (in press).

Irikura, K.K., and Goddard, W.A. III, **"Energetics of Third-Row Transition Metal Methylidene Ions MCH_2+ (M = La, Hf, Ta, W, Re, Os, Ir, Pt, Au),"** J. Am. Chem. Soc. 116, 8733 (1994).

Irikura, K.K., Hudgens, J.W., and Johnson, R.D. III, **"Spectroscopy of the Fluoromethylene Radicals HCF and DCF by 2 + 1 Resonance Enhanced Multiphoton Ionization Spectroscopy and by ab Initio Calculation,"** J. Chem. Phys. 103, 1303 (1995).

Jacox, M.E., Irikura, K.K., and Thompson, W.E., **"Matrix Isolation Study of the Interaction *of Excited Neon Atoms with SiF_4. Infrared Spectra of SiF_3^+ and SiF_3^-,"*** J. Chem. Phys. (in press).

Johnson, R.D. III, ***"FO^+ and FO ab initio Vibrational Constants,"*** Chem. Phys. Lett. (in press).

Johnson, R.D. III, and Irikura, K.K., ***"Excited Electronic States of PF_2,"*** Chem. Phys. Lett. 228, 273 (1994).

6. *Quality Control and Software Development for the NIST/EPA/NIH Mass Spectral Database*

S.E. Stein, C.L. Clifton, S.G. Lias, O.V. Fateev (Russian Academy of Sciences, Russia), A.A. Levitsky (Institute of Organic Chemistry, Russia), A. I. Mikaya (Topchiev Institute of Petrochemical Synthesis, Russia), T.F. Levitskaia (Moscow Institute of Radiotechniques, Russia), B. Yang (Dalian Institute of Chemical Physics, China), R. Mistrik (University of Vienna Institute of Analytical Chemistry, Austria), A.J. Lysak (Dept. of Aviation Industry, Russia), V.V. Andreev (Institute of Aircraft Equipment, Russia) and P. Ausloos (Guest Researcher)

Objective: To maintain and improve the quality of the NIST/EPA/NIH Mass Spectral Database, a database of 75,000 mass spectra of 62,235 compounds used in the data systems of more than 14,000 commercial mass spectrometers; to produce the personal computer version of the database, and evaluate/develop software for using/manipulating mass spectral data.

Problem: The Mass Spectral Database was developed by scientists at the EPA and NIH in the early 1970s, and was maintained until 1988 at the EPA, but was distributed by the NIST(NBS) Standard Reference Data Program starting in 1978. In 1988, after several articles appeared pointing out the poor quality of the database, it was moved into NIST and the Mass Spectrometry Data Center was created to maintain and improve it. An extensive evaluation effort has weeded out thousands of poor quality spectra, and improved algorithms and software for use with mass spectral data have been developed.

Approach: In addition to work aimed at increasing the size of the data collection, which is described as a separate project, the Data Center has two primary functions: (1) the evaluation of both the new data and all of the collected data to eliminate errors, and/or prevent the addition of erroneous spectra to the database; (2) the development of better tools to utilize the data and extract more information from the data.

Results and Future Plans: In 1995, the long-term evaluation of all the spectra in the database continued. The first milestone associated with this effort, the evaluation of all replicate spectra in the collection and release of a database including evaluated replicates, was finished and released as part of Version 4.5. The second milestone, the evaluation of all the spectra in the entire collection, is within a few months of being complete. Numerous problems and errors have been identified and the problem spectra have been deleted from the collection, or appropriate corrections have been made. The major improvement in the quality of the NIST/EPA/NIH Mass Spectral Database as a result of the systematic evaluation effort is widely recognized by the database user communities.

In 1995, a new personal computer version of the database for use with Microsoft Windows was released. This major effort, which had been under preparation for two years, provides new search systems, optimized spectrum matching algorithms, and many other new features which increase the flexibility and efficiency of use of the database. Other developmental work addressed (a) making correlations between substructural elements in the molecules and details of the corresponding mass spectra, and (b) research on algorithms used for matching unknown spectra and interpreting mass spectra. On-going work is aimed at developing an algorithm that uses the apparent structure of a molecule to predict every peak in the spectrum. The expectation from this work is that the algorithms developed can be inverted to provide better prediction of the structure from a spectrum of an unknown compound.

Publications:

Ausloos, P., Clifton, C.L., Fateev, O.V., Levitsky, A., Lias, S.G., Mallard, W.G. Shamim, A., and Stein, S.E., **"NIST Mass Spectral Search Program and the NIST/EPA/NIH Mass Spectral Library,"** NIST Standard Reference Database 1A, (1995).

Emery, S.L., Stein, S.E., Lewis, M., Kassel, R., and Piffath, R., **"A Masked GC/MS Database for Verifying the Chemical Weapons Convention and Protecting Confidential Business Information,"** Proceedings of 3rd International

Conf. on On-Site Analysis, January 1995, Houston, TX

Stein, S.E., **"An Analysis and Optimization of Mass Spectral Library Search Algorithms,"** Proceedings of the 42nd ASMS Conference on Mass Spectrometry and Allied Topics, 17 (1994).

Stein, S.E., **"Chemical Substructure Identification by Mass Spectral Library Searching"**, J. Am. Soc. Mass Spectrom. (in press).

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7. *Acquisition of New Spectra for the NIST/EPA/NIH Mass Spectral Database and the NIST/EPA Vapor Phase Infrared Database*

C.L. Clifton and S.E. Stein

Objective: To acquire new spectra for the Mass Spectral Database and the Vapor Phase Infrared Database, either by in-house experimental determination or by the acquisition of collections of high quality data determined elsewhere. In particular, the objective is to acquire spectra of all commercially-available compounds or other compounds of importance for industrial or environmental reasons.

Problem: When NIST acquired the task of maintaining and advancing the Mass Spectral Database in 1988, the size of the collection of spectra had not increased for several years. The mass spectrometry community had begun to regard the database as moribund. Furthermore, at that time many compounds that are widely-used or important for other reasons were not represented by spectra in the database.

Approach: Because of the need to acquire thousands of mass spectra of commercially-important compounds, a project aimed at enlarging the database through the laboratory determination of targeted spectra was initiated. Other efforts were made to locate and purchase large pre-existing collections of high quality spectra. The mass spectrometric instrument used for the project is capable of simultaneously producing an infrared spectrum of the compound, and therefore, the NIST/EPA Vapor Phase Infrared Database is produced as a spin-off of the Mass Spectral Database.

Results and Future Plans: When the Mass Spectral Database was moved to NIST in 1988, it contained 42,000 spectra; the 1996 release will include more than 100,000 spectra. Twelve hundred mass spectra and infrared spectra were determined in the laboratories of the Data Center in 1995. Through a contract with NIH, original spectra of a large collection of medically relevant compounds are also being determined for the database, and a

laboratory in England is determining new spectra of derivitized compounds for the database. These compounds are used for analysis of medically important compounds, as well as several important classes of compounds (including pesticides) that are difficult to pass through a chromatographic column in an un-derivitized state. A collection of 17,000 high quality spectra has just been acquired from the Japanese National Labs and a collection of 30,000 spectra is being acquired from Chemical Concepts in Germany. Work is now being initiated to obtain Chemical Abstract Registry Numbers, names and synonyms, and to make structural drawings of these compounds, so that all the new spectra can be added to the distributed database.

The mass spectra and infrared spectra acquired are processed for the databases by retrieving of Chemical Abstracts Registry Numbers for each compound, producing structural drawings, and entry of names and synonyms into a database. Each spectrum is examined by an expert mass spectrometrist before being included in a database.

Publications:

Clifton, C.L., Shamim, A., Nayak, K., Mikaya, A., and Stein, S.E., "**Problems and Progress in the Measurement of Reference Mass Spectra,**" Proceedings of the 42nd ASMS Conference on Mass Spectrometry and Allied Topics, 17 (1994).

8. *The Structures & Properties Data Project*

***S.E. Stein**, W.G. Mallard, H.Y. Afeefy (Univ. of Maryland Baltimore County), O.V. Fateev (Russian Academy of Sciences, Russia), A.A. Levitsky (Institute of Organic Chemistry, Russia), J.F. Liebman (Univ. of Maryland, Baltimore County), Y.-R. Luo (Univ. of Ottawa, Canada), D.V. Tchekhovskoi (Institute for High Temperature, Russia), and Y.A. Mirokhin (Institute of Avionics, Russia)*

Objective: To collect and evaluate a large body of data on various chemical and physical properties for distribution as part of the Structures & Properties database; to develop structure-based estimation schemes for these properties.

Problem: Four years ago, the generic chemical database software known as "Structures & Properties" was released for distribution to the public with a small database of organic thermochemical data originally developed for use with the Ion Energetics database. The Structures & Properties software provides the user with the capability to make structure-based estimations, and also functions as a powerful front-end for chemical databases that can be searched by structure or substructure, formula, name or synonym, or Chemical Abstracts Registry Number. Since the initial release, a major goal of the project has been to collect and evaluate a large body of data on chemical and physical properties for inclusion with the database, and for use in the development of improved estimations of properties.

Approach: Several sub-projects aimed at developing specialized databases for use with the Structures & Properties Software are proceeding through traditional database-building activities, involving scanning the technical literature and retrieving all numeric data found there. Databases being built include: enthalpies of formation of organic compounds, chromatographic retention indices, Henry's Law Constants, and boiling points.

Results and Future Plans: The long-term effort aimed at providing the first *complete* collection of data on the enthalpies of formation of organic

compounds is close to completion, and will be included in a new release of Structures & Properties. All calorimetric data published from the time of the beginning of Chemical Abstracts to the present have been abstracted and entered into a computer file. The collection includes data on about 6,000 organic compounds. In addition, data on several thousand retention indices have been abstracted, evaluated, and entered into a computer file for inclusion in the next release. Future work will involve collecting all the data on enthalpies of formation of transient species derived from kinetic (rather than calorimetric) measurements, and incorporation of a large database of evaluated enthalpies of formation of organometallic compounds being acquired from a scientist in Portugal.

A new, physically reasonable approach involving the initial prediction of vapor pressures has been developed for the prediction of boiling points. Earlier approaches developed under this project have been chosen by DIPPR as the currently most reliable way of predicting boiling points; the new algorithms being developed will provide improved reliability in predicted boiling point data.

Publications:

Luo, Y.-R., Holmes, J.L., and Stein, S.E., **"Homo- and Heterolytic X-C Bond Energies. Part III. Heterolytic Bond Energies in Cycloalkyl Compounds,"** Proceedings of the 42nd ASMS Conference on Mass Spectrometry and Allied Topics, 17 (1994).

9. Development of Mechanisms for Electronic Access to NIST Chemical Reference Data for Industry

W.G. Mallard

Objective: Develop interface to permit making NIST chemical reference data available on the Internet, especially for industrial users.

Problem: This project, supported by the larger Systems Integration for Manufacturing Applications (SIMA) Project, is aimed at providing the mechanisms needed to make NIST chemical reference data available on the Internet.

Approach, Results, and Future Plans: During FY95, an Internet interface was completed to allow users access to a compilation of chemical names and structures for which information is provided in NIST databases. The user is able to enter a query about particular chemical species (a formula or a Chemical Abstracts Service Registry Number), and retrieve a list of compounds that match that formula, and learn what kinds of data concerning the particular species are available in NIST databases.

10. *Characterization of Nonthermal Plasma Chemistry through Kinetics Measurements*

J.W. Hudgens, R.D. Johnson III, L.W. Sieck, D.S. Green (Stanford Univ.) and J.T. Herron (Guest Researcher)

Objective: To develop advanced diagnostic tools for studying plasma chemistry, and to characterize the nature of chemical reaction mechanisms in plasmas with the aim of optimizing the conditions for plasmas used for material processing (etching and deposition), and for the abatement and remediation of gaseous pollutants.

Problem: Advances in effective manufacturing and environmental cleanup can be achieved by exploiting nonthermal plasmas. In such discharges, chemical change is driven by a variety of processes including ionization, molecular excitation, ion-electron recombination, fragmentation of ions and excited molecules, and reactions of radicals and ions. Control and optimization of plasma processing requires a quantitative understanding of these events under reproducible conditions.

Approach: This project, now in its second year, involves the development of *in situ* diagnostics combined with effluent analysis and kinetic modeling to characterize reactive species and processes occurring in the plasmas. The optical facility is designed to be flexible, and can be used with degenerate four-wave mixing (DFWM) spectroscopy, laser-induced fluorescence (LIF), cavity ring down (CRD) and other forms of laser-based diagnostics. In addition to corona and microwave discharge systems, a standard plasma reactor, a second-generation Gaseous Electronic Conference (GEC) Reference Cell is being constructed. The GEC cell is needed for achieving standard conditions so that data acquired in different laboratories can be readily compared.

Results and Future Plans: The pilot studies used DFWM to detect Ar* metastables in Ar/molecule discharges, a system of interest because argon is one of the most common carrier gases for reactive plasmas, and Ar* species participate in collisional energy transfer, charge transfer, and promotion of molecular decomposition. The first DFWM studies of molecules investigated CH($A\ ^3\Pi$), NH($A\ ^3\Pi$), OH($A^2\Sigma^+$), and BH($A^1\Pi$) radicals in the microwave discharge flow reactor. These diatomic species are common intermediates in reactive discharges and are often the standard for diagnostics and modeling of concentration and temperature. Current efforts reflect a shift toward kinetic and mechanistic studies involving these intermediates in industrial processes.

Initial material processing studies involved examining BH and NH radicals in a flowing microwave discharge in order to understand downstream plasma deposition of boron nitride (BN) coatings, and the use of boron trichloride (BCl_3) in semiconductor and metal etching. Studies of dilute mixtures of boron trichloride with either ammonia (NH_3) or N_2 and H_2 in argon were carried out in a discharge reactor, and the relative concentrations of radical intermediates were monitored as a function of flow rate, pressure, mixing ratio, power coupled into the plasma, and position relative to the microwave applicator. Under certain mixture and flow conditions, hard coatings were deposited on downstream surfaces.

The nature of chemical mechanisms in the partial oxidation of pollutants has been examined by probing the plasma degradation of aromatic hydrocarbons such as toluene. This chemistry is complicated by the role of humid air, which is of central concern in applications such as treatment of diesel exhaust. The targeted intermediates include OH, CH. methylene (CH_2), and methyl (CH_3) radicals generated in corona and microwave discharge flows of nitrogen or air contaminated with toluene and water. Future *in situ* experiments will provide temperature and concentration profiles for comparison with studies of the terminal ion chemistry, as well as quantitative analysis of effluents; the evolution of the species distribution is also needed to test kinetic models and evaluate mass balance. Spatial profiles of the OH radical distribution as a function of water content reveal that the characteristics of the discharge and the chemical processes occurring are significantly affected by the presence of moisture. Auxiliary studies carried out in the Division's high pressure pulsed electron beam mass spectrometer permit a

detailed understanding of the ion chemistry occurring in such systems, particularly the clustering of water molecules with ionic species. The reaction sequence has been modeled and calculated using the Acuchem program and a select set of important reactions and rate constants.

Publications:

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Green, D.S., Sieck, L.W., and Herron, J.T., **"Characterization of Chemical Processes in Non-thermal Plasmas for the Destruction of Volatile Organic Compounds,"** Proceedings of the 12th International Symposium on Plasma Chemistry, August 1995, Minneapolis, Minnesota, p. 965.

Green, D.S., Sieck, L.W., and Herron, J.T., **"Characterization of Chemical Processes in Non-thermal Plasmas for the Destruction of Volatile Organic Compounds,"** Proceedings of the International Symposium on Environmental Technologies - Plasma Systems and Applications, October 1995, Atlanta, Georgia.

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Pearson, J., Dixon, R.N., Hudgens, J.W., and Russell, R.D. III, **"Resonance Enhanced Multiphoton Ionization Spectroscopy of the SNF Radical"**, Chem. Phys. Lett. (in press).

11. High Temperature Kinetics Studies

***J. Manion**, W. Tsang, J. Herzler (DLR Stuttgart, Germany) and K.K. Balasubramanian (Indian Institute of Technology, India)*

Objective: To develop a fundamental quantitative understanding of high temperature reactions of organic compounds with the goal of achieving a complete understanding of large scale chemical phenomena such as combustion or flame inhibition.

Problem: A complete understanding of large-scale chemical phenomena, such as combustion, requires quantitative information about the relevant elementary thermal reactions. The focus of this long-term project is to provide high quality experimental data on the rates and mechanisms of chemical reactions. Such data are critical inputs to fundamental reaction models that are increasingly being used to understand and ultimately control reaction efficiencies and pathways in chemical systems. Of current interest are problems related to the combustion of fuels and the combustion of halocarbons associated with flame inhibition and waste incineration. Other recent studies deal with the decomposition of compounds of interest to the semiconductor industry (such as tetraethoxysilane - TEOS - which is used to lay down the dielectric film SiO_2), and of model compounds related to the destruction of stockpiles of chemical warfare agents.

Approach: Experimental investigations are carried out in a unique heated single-pulse shock tube. The shock tube is heated to allow introduction of compounds of low volatility. The shock tube itself rapidly shock-heats the sample to allow the investigation of its high temperature chemical properties.

Results and Future Plans: Most of the currently used fire suppressants and suggested short-term replacements involve organic compounds with C-F bonds. When used as fire suppressants, such compounds will be subject to high temperatures, and therefore their high temperature decomposition processes must be understood. Recent experimental results demonstrated that previously accepted values for rates of hydrogen atom attack on C-F bonds were orders of magnitude too high.

Destruction pathways for aliphatic fluorine-containing compounds are now understood to be vastly different from those for hydrocarbons, where decomposition is frequently initiated by radical attack on the C-H bond. The detailed quantitative information obtained allows the prediction and design of compounds with particular "windows" of thermal stability. In contrast to aliphatic fluorocarbons, aromatic fluorocarbons are found to undergo defluorination by hydrogen atoms, probably through displacement; this reaction had previously been believed not to occur. A major consequence is that free atomic fluorine will be released into reacting systems containing aromatic fluorocarbons; the formation of unwanted toxic byproducts in the destruction of fluorocarbons may result.

Kinetic and mechanistic studies of theunimolecular decomposition of TEOS, and its reactions with radicals such as the hydrogen atom, have shown the occurrence of processes leading to the formation of ethene, silanols, and ethanol, which could play major roles in industrial reactors depositing SiO_2 films. Similar studies on oxygen-containing organic compounds which are in use as gasoline additives suggest that four-center eliminations, radical attack, and bond fission reactions are important under conditions related to the use of oxygenates as gasoline additives and "clean fuel" alternatives. Future work includes further systematic examinations of these kinds of system, as well as studies of processes responsible for the formation of polyaromatic hydrocarbons and soot. Increasingly stringent clean air standards mean that a better understanding of such processes will be needed in order to control and reduce the formation of such pollutants in combusting systems.

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12. *Condensed Phase Kinetics*

***P. Neta**, R.E. Huie, J. Grodkowski (Institute of Nuclear Science, Warsaw, Poland), G. Khaikin (Institute of Electrochemistry, Russia), and Z.B. Alfassi (Ben Gurion Univ., Israel)*

Objective: To elucidate the individual steps in reaction mechanisms occurring in the condensed phase. Particular attention is given to (a) reactions pertinent to the conversion of solar energy into chemical energy; that is, of reactions important in the catalytic oxidation of water to oxygen and the reduction of water to hydrogen in the presence of metalloporphyrin photosensitizers; and to (b) the reactions of radicals that are important because of their role in the environment (acid rain formation, for example) and in industrial chemical processes.

Problem: The conversion of solar energy into chemical energy is accomplished by plants through the process known as photosynthesis, in which chlorophyll, a pigment which absorbs energy from the sun, harnesses solar energy. Metalloporphyrins, which have broad absorption spectra in the visible light range and also display rich redox chemistry, are efficient photosensitizers for solar energy conversion and storage. Under research sponsored by the Department of Energy metalloporphyrin chemistry is explored in order to find conditions/catalysts to enable these compounds to perform the same function as chlorophyll, since chlorophyll is unstable and cannot be used in industrial environments. Related studies of peroxyl radical reactions focus mainly on arylperoxyl radicals, including polychlorinated aromatics whose peroxyl radicals may be formed during oxidative decomposition of these hazardous waste materials.

Approach: Experiments elucidate individual steps in complex reaction mechanisms using pulse radiolysis and laser flash photolysis techniques for the rapid generation of reactive intermediates which are subsequently detected by optical techniques.

Results and Future Plans: Studies of the reduction and alkylation reactions of metallo-porphyrins that may be important as catalysts for reduction or binding of carbon dioxide were continued. Studies of Rh porphyrins by radiation chemical and photochemical techniques revealed the mechanisms of reaction of several intermediate species, indicating production of hydrogen, but little reduction of carbon dioxide. The results suggest that carbon dioxide reduction by these porphyrins may happen in heterogeneous systems, but not in homogeneous solutions. Cyclic voltammetry experiments also did not indicate efficient catalysis of CO_2 reduction by Rh-porphyrins. Studies of iron porphyrins have been initiated.

The effect of halogen substitution on the reaction kinetics of arylperoxyl radicals was examined, and the effect of solvent on the rate constant for oxidation by the radicals was systematically traced. The reactions of several alkyl- and aryl-peroxyl radicals with ferrous and ferrocyanide ions were found to show different behavior for the two ions. The reaction with ferrocyanide is an outer-sphere electron transfer whose rate constant is controlled by the driving force and thus dependent on radical structure and substitution, whereas the reaction with ferrous ion is by an inner sphere mechanism forming an intermediate complex in a process whose rate is dependent on the rate of water exchange, not on the oxidative power of the peroxyl radical.

In 1995, a linear accelerator (LINAC) was purchased from Ohio State University, and installation at NIST was initiated. The instrument will provide repeating 4-5 MeV electron pulses with a peak current of 150 to 450 ma and with time duration from 20 to 1400 ns. The new facility will expand the capabilities of this project, for instance, permitting for the first time signal averaging so that radicals with weak optical absorptions can be studied.

Publications:

Alfassi, Z.B., Huie, R.E., Marguet, S., Natarajan, E., and Neta, P., **"Rate Constants for Reactions of Iodine Atoms in Solution,"** Int. J. Chem. Kinet. 27, 181 (1995).

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Khaikin, G.I. and Neta, P., **"Formation and Reactivity of Vinylperoxyl Radicals in Aqueous Solutions,"** J. Phys. Chem. 99, 4549 (1995).

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13. Atmospheric Kinetics: Determinations of the Stability of Halocarbons in the Atmosphere

M.J. Kurylo, R.E. Huie, T.J. Buckley, A. Fahr, P. Neta, B. Laszlo (Hungarian Academy of Science, Hungary), A.K. Nayak (Bhaba Atomic Research Center), and V. Orkin (Russian Academy of Science, Russia)

Objective: To study the gas phase kinetics and photochemistry of important atmospheric constituents in order to generate data relevant to predicting the impact of human activities on stratospheric ozone and on global climate.

Problem: In 1974, M. J. Molina and F. S. Rowland suggested that chlorine atoms produced by photochemical degradation of chlorofluorocarbons (CFCs) in the upper atmosphere could lead to a depletion of the earth's protective ozone layer. In the years since, an important activity in the gas phase kinetics community has been to develop experimental data and models used to understand and predict those processes relevant to the fate of natural and anthropogenic trace gases in the troposphere and their chemical role in altering stratospheric composition. Other in-house experimental work involves determinations of the absorption cross sections of relevant molecules in the far ultraviolet and ultraviolet in order to determine the photolytic lifetimes of molecules in the upper troposphere and lower stratosphere. This project provides original experimental measurements relevant to the problem of ozone depletion, working in tandem with the data evaluation efforts of the Chemical Kinetics Data Center (described above).

Approach: Both flash and laser photolysis resonance fluorescence techniques are used to generate radicals of interest and monitor their reaction kinetics. An improved experimental facility permits the precise determination of rate constants as small as 10^{-16} cm^3 $molecule^{-1}$ s^{-1}. Using an approach developed in this laboratory for the determination of especially low cross sections by making measurements in the liquid phase, the temperature dependences of the absorption cross sections of the alternate halocarbons are determined.

Results and Future Plans: Rate constants have been determined for the reactions of OH radicals with compounds under consideration as industrial replacements for the fully-halogenated chlorofluorocarbons (CFCs). In addition, studies this year have used excimer laser photolysis dual wavelength kinetic absorption spectroscopy to elucidate radical-radical reactions, focussing on chain-carrying processes in bromine and iodine catalytic cycles for ozone destruction. Rate constants for the reactions ($O + I_2$), (O + IO) and (IO + IO) were determined, as well as several reactions in the (IO + BrO) kinetic system. A productive series of studies on the atmospheric chemistry of chemicals under consideration for use as automobile fuel additives continued this year in collaboration with researchers at the Ford Motor Company. Ultraviolet absorption cross-sections were determined this year for methyl chloroform, methyl iodide, CF2ClCH3 (HCFC-142b), and CF_3CCl_2H (HCFC-123).

The collaborative work with researchers at Brookhaven aimed at determinations of bond strengths in halocarbon compounds led this year to new measurements that permitted an evaluation of the bonds strengths $D°_{298}$ (F-CFO) and $D°_{298}$ (F-CO). Carbonic difluoride (CF_2O) and the fluorooxomethyl radical (FCO) are important intermediates in the oxidative degradation of many fluorinated compounds, and are involved in the mechanism of flame suppression by fluorinated compounds. High level *ab initio* calculations carried out by Division member R.D. Johnson contributed to the evaluation of the experimental data.

Publications:

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14. Kinetics of Reactions Relevant to Planetary Atmospheres

A. Fahr, A.K. Nayak (Bhaba Atomic Research Center), and A. Laufer (U.S. Dept. of Energy)

Objective: To elucidate the reaction kinetics of radicals thought to play a role in carbon-rich atmospheres.

Problem: Unsaturated hydrocarbon radicals play an important role in the atmospheres of the outer planets, and an understanding of their chemistry permits an understanding of those atmospheres. In addition, the temperature dependences of absorption cross sections of unsaturated hydrocarbons and inorganic gases present in planetary atmospheres are determined. Such results, which may permit correct interpretation of the ultraviolet spectroscopic data obtained from earth-orbiting satellites and telescopes or interplanetary probes, are badly needed because of a serious gap in the knowledge base. The project has been supported for several years by the NASA Planetary Atmospheres Program.

Approach: Flash photolysis and laser photolysis resonance fluorescence techniques are used. Temperature dependences of absorption cross sections of unsaturated hydrocarbons are also determined.

Results and Future Plans: Investigations were initiated on the photolytic production, spectroscopic detection, and reaction kinetics of the propargyl (C_3H_3) radical. Despite their importance in both planetary atmospheres and in combustion, relatively little is known about the reaction kinetics and spectroscopy of these radicals. All the major products of the propargyl radical combination reactions have been identified and quantified. Preliminary results suggest a rate constant of about 10^{-10} cm^3 $molecule^{-1}$ s^{-1} for the propargyl combination reaction which leads to the formation of three C_6H_6 isomers. Also, a transient absorption at about 250 nm was detected and predicted to originate from an electronic transition in the propargyl radical.

Publications:

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15. *Calorimetric Measurements for Industry*

***D.R. Kirklin**, P.A.G. O'Hare, D.G. Archer, and I. Zieborak-Tomaszkiewicz (Institute of Physical Chemistry, Poland)*

Objective: To make experimental determinations of standard molar enthalpies of formation and heat capacities of industrially-important compounds.

Problem: A key thermodynamic property of all substances is the standard molar enthalpy of formation, which is necessary to evaluate the molecular energetics of important materials and the thermodynamic feasibility of their chemical reactions. When measurements of standard molar enthalpies of formation are combined with data on heat capacities, equilibrium constants for systems of interest can be predicted. An industrial consortium, the Design Institute for Physical Property Data (DIPPR), has identified a number of industrially-important chemicals for which thermochemical data are needed. The focus of the work of the laboratory is to provide such quantititative information needed by industry. Other work is aimed at determining enthalpies of formation of "high tech" materials, which are often amorphous (glassy) and cannot be determined by standard techniques involving burning the substance in oxygen.

Approach: The Division has two calorimetry laboratories devoted to providing experimental determinations of standard molar enthalpies of formation of pure substances, and a laboratory for heat capacity determinations. The precision oxygen bomb calorimetry laboratory has unique well-characterized calorimetry equipment which is capable of making combustion measurements on samples as small as 10-15 milligrams, permitting routine measurements on substances which are available only in small quantities. Differential scanning calorimetry provides auxiliary information on sample purity, enthalpies of fusion, heat capacities, and melting temperatures. The Division's fluorine bomb calorimetry facility, which is the only operating facility of its kind in the world, uses the exceptional oxidizing power of high-pressure fluorine to allow the determination of thermochemical information for compounds that cannot be burned in oxygen.

Results and Future Plans: Industrially-important compounds are often not available as research grade chemicals, and this problem was addressed in 1995 with work on the design of methods to purify and determine sample purities. The capabilities of the oxygen-bomb calorimetry laboratory were expanded to include routine differential scanning calorimetric (DSC) measurements, and a project was designed to certify two standards that could be used to calibrate DSC instruments. The thermochemical properties of acetylsalicylic acid (aspirin), acetamidophenol (tylenol), and 2-(4-isobutylphenyl)propanoic acid (ibuprophen) were determined for DIPPR.

In 1995, fluorine bomb calorimetric determinations were completed on the materials: W_5Si_3, Mo_5Si_3, $Se_4(AsF_6)_2$, and SiS_2. The fluorine-bomb calorimetry work is closely allied to the evaluation of inorganic thermochemical data under the NIST/JANAF Thermochemical Tables Project, described above. Systematic determinations of the thermal properties of metal silicide compounds in the Division's heat capacity facility continued this year with studies of Ti_5Si_3(cr) and $TiSi_2$(cr). Highly accurate heat capacities were obtained from enthalpy increments determined for these compounds as well as for bismuth(cr). The latter study made possible the resolution of discrepancies in the literature concerning the thermodynamic properties of bismuth.

Publications:

Archer, D.G., **"Enthalpy Increment Measurements from 4.5 to 318 K for Bismuth (cr). Thermodynamic Properties from 0 K to the Melting Point,"** J. Chem. Engr. Data 40, 1015 (1995).

Archer, D.G., Sabella, M.S., Stillman, S.E., and Cotts, E.J., **"Enthalpy Increment Measurements from 4.5 to 350 K and the Thermodynamic Properties of Titanium Disilicide(cr) to 1700 K,"** J. Chem. Engr. Data (in press).

O'Hare, P.A.G., **"Thermochemical Studies of Inorganic Chalcogenides by Fluorine-Combustion Calorimetry. Binary Compounds of Germanium and Silicon with Sulfur, Selenium, and Tellurium,"** Thermochimica Acta (in press).

O'Hare, P.A.G., Volin, K.J., and Susman, S., **"Thermochemistry of (Germanium + Sulfur). III. Massic Energies of Combustion in Fluorine and the Derived Standard Molar Enthalpies of Formation of Crystalline and Vitreous Germanium(IV) Disulfide GeS_2 at the Temperature T = 298.15 K. Standard Molar Enthalpy of the Transition GeS_2(cr) = GeS_2(vit) at T = 298.15 K. Critical Assessment of Thermodynamic Quantities for the High-Temperature Reaction: GeS_2(cr) = GeS(g) + ½S_2(g),"** J. Chem. Thermodyn. 27, 99 (1995).

Tomaszkiewicz, I., Hope, G.A., Beck, C.M. II, and O'Hare, P.A.G., **"Thermodynamic Properties of Silicides. IV. Determination of the Standard Molar Enthalpies of Formation at the Temperature 298.15 K of Pentatungsten Trisilicides of Composition W_5Si_3 and $W_5Si_{3.115}$ by Fluorine-Combustion Calorimetry,"** J. Chem. Thermodyn. 27, 585 (1995).

Tomaszkiewicz, I., Hope, G.A., and Beck, C.M. II, and O'Hare, P.A.G., **"Thermodynamic Properties of Silicides. V. Trimolybdenum Monosilicide Mo_3Si. Fluorine-Combustion Calorimetric Determination of the Standard Molar Enthalpy of Formation at the Temperature 298.15 K, and a Critical Assessment of the Molar Heat Capacity, Molar Enthalpy Increments, and Molar Gibbs Free Energy of Formation,"** J. Chem. Thermodyn. (in press).

Tomaszkiewicz, I., Hope, G.A., and O'Hare, P.A.G., **"Thermochemistry of (Germanium + Tellurium) I. Standard Molar Enthalpy of Formation $\Delta_f H_m^\circ$ at the Temperature 298.15 K of Crystalline Germanium Monotelluride GeTe by Fluorine-Bomb Calorimetry. A Critical Assessment of the Thermodynamic Properties of GeTe(cr and g) and $GeTe_2$(g),"** J. Chem. Thermodyn. 27, 901 (1995).

Tomaszkiewicz, I., Susman, S., Volin, K.J., and O'Hare, P.A.G., **"Fluorine-Combustion Calorimetric Determinations of the Standard Molar Enthalpy Changes for the Formation of $SiSe_2$, $SiSe_{1.94}$(cr) and $SiSe_{1.94}$(vit), and for the Transition $SiSe_{1.94}$(vit) = $SiSe_{1.94}$(cr) at the Temperature T = 298.15 K. Implications of the Results for the Enthalpies of Dissociation D°(Se-SiSe) and D°(SiSe). Thermodynamic Properties of SiSe(g),"** J. Chem. Thermodyn. 27, 585 (1995).

16. *Determination of Thermodynamic Data for Aqueous Terrestrial Processes at Subfreezing Temperatures*

R.W. Carter *and D.G. Archer*

Objectives: The determination of thermodynamic data on aqueous solutions of acids, salts and related mixtures in the temperature range from 180 to 300K.

Problem: Chemical thermodynamic data on aqueous solutions below the freezing point of water are relevant to understanding and predicting processes such as freezing, thawing, heaving, dissolving, precipitating, mixing and transport, as well as for an understanding of the heterogenous chemistry occurring in the atmosphere on the surface of ice crystals. The low temperature data on aqueous salt solutions have applicability to engineering problems in cold regions, de-icing of roads with salts, and separation of salts in cold environments. Low temperature data on nitric acid have applicability to simulation and modeling studies of heterogeneous nucleation processes for the formation of nitric acid trihydrate in the stratosphere. In general, thermodynamic data on aqueous solutions are abundant for the temperature range above room temperature (300 to 600K), but are almost non-existent for lower temperatures.

Approach: Differential scanning calorimetry, and a newly constructed flow calorimeter are used.

Results and Future Plans: A differential scanning calorimeter (DSC) was used to measure the heat capacities of aqueous sodium chloride solutions at molalities from 0.05 to 6.0 $mol \cdot kg^{-1}$ and temperatures from 190 to 300K at a pressure of 0.1 MPa. The DSC measurement permits solutions to be supercooled to temperatures below their normal freezing points before crystallization occurs. Bulk solutions were cooled approximately 20K below their freezing points. Emulsions of aqueous NaCl in an organic phase of n-heptane with 4% sorbitan tristearate were prepared. The emulsion droplets ranged in size from 1-5 μm and allowed cooling approximately 40K below their freezing points. The accuracy of the heat capacities at constant pressure is estimated as 0.3% for the bulk solution results and 0.5 to 0.75% for the emulsion results. The results show an extreme dependence of the apparent molar heat capacities versus temperature as the degree of supercooling increases. Future plans are to continue work with determinations of the properties of super-cooled solutions of $NaNO_3$, $ZnCl_2$, $Zn(NO_3)_2$, and HNO_3.

III. Process Measurements Division (836)

Gregory J. Rosasco, Chief

A. Division Overview

Mission:
The Process Measurements Division develops and provides measurement standards and services, measurement techniques, recommended practices, sensing devices, instrumentation, and mathematical models required for analysis, control, and optimization of industrial processes. The Division's research seeks fundamental understanding of, and generates critical data pertinent to, chemical process technology. These efforts include the development and validation of data-predictive computational tools and correlations, computer simulations of processing operations, and provision of requisite chemical, physical, and engineering data.

Programs:
Process and quality control require calibration of instruments against, or use of procedures traceable to, national standards. Therefore, **measurement standards and calibration services** represent a very important part (over 40%) of our activities. We provide support critical for **temperature, humidity, fluid flowrate, air speed, and liquid density and volume measurements** with more than 800 standard tests and calibrations performed this year. The Division's commitment to provision of these services involves many facets: the establishment, maintenance, and improvement of the primary standards; continuing intercomparisons of these standards to those of other nations; development of suitable mechanisms for transferring the requisite measurement accuracy to customers in the field and in secondary calibration laboratories; and continual attention to service efficiency and measurement quality.

While these measurement and calibration services are provided to a wide range of customers, we also have measurement support programs focussed on specific strategic technologies, such as maintaining U.S. leadership in semiconductor device manufacturing. As part of NIST's National Semiconductor Metrology Program (NSMP), the Division is selecting, developing, evaluating, and validating **process measurement technologies important in semiconductor manufacturing**. In FY95, these efforts included development of improved thermocouples, low gas-flowrate calibrations (joint with the Thermophysics Division), methods to determine plasma electrical properties (joint with the Electronics and Electrical Engineering Laboratory and the Physics Laboratory), *in situ* optical measurements of chemical species in thermal and plasma processing reactors, and very low-level moisture measurements for contamination control in process gases (joint with the Thermophysics Division). In these efforts we typically make use of a reference chemical processing reactor prototypical of industrial manufacturing environments. This allows critical tests of the measurement approach and its utility for the intended application. Because processing systems are typically complex, with strongly coupled chemistry and mass transport characteristics, reference reactors are subject to extensive modeling and validation efforts as an integral part of the measurement support activity. These models and supporting data play a critical role in all elements identified by the Semiconductor Industry Association's (SIA) National Technology Roadmap for Semiconductors. In fact, modeling is specifically identified not only as a "crosscutting technology" but as "pervading all crosscuts". Our program in this area, partially supported by NIST's NSMP, seeks to develop **benchmark chemical mechanisms and supporting thermochemical and kinetic data, for equipment and process design**. These chemical mechanisms must be integrated with appropriate transport models and simulations, and validated to meet the needs of our industrial customers. Again, reference reactors serve as vital testbeds for validating these models. These two semiconductor-related programs constitute about 20% of the Division's work.

The technical approach described above, which emphasizes measurement technology development, provision of process models and supporting data, and validation on prototypical systems, characterizes not only our semiconductor-related efforts, but also is representative of our **process technologies** thrust. Key components of this thrust are our materials chemistry, spray combustion, and hydrothermal oxidation programs (together comprising about 20% of the Division). The first of these, highly synergistic with the semiconductor models and data program, develops **chemical and process models and data to support the production of high technology materials**. In a project joint with the Materials Science and Engineering Laboratory, we are studying multiphase combustion (oxidation) synthesis of nanoscale magnetic oxides, important for information storage technology. A second part of the program looks at the use of a sodium burner to synthesize metals and non-oxide ceramics, e.g., Ti and TiB_2, required for high-temperature, high-strength applications in the aerospace industry. This novel processing method offers a relatively low temperature (low energy consumption) route with promise for bulk-synthesis of these generally difficult-to-prepare materials. It also has the advantage of essentially zero emissions providing an inherently "green" processing approach for the production of high technology materials.

Addressing industrial problems associated with the operation and design of thermal reactors is the main focus of the other two Division programs in process technology. Based upon unique spray measurement capabilities (optical measurements of droplet size and velocity distributions) and a spray combustion facility, the first program emphasizes measurement of the role of droplet dynamics (generation, transport, and mixing) in determining the performance (efficiency and emissions) of spray-based energy production and waste destruction systems. The initial objective of this effort is to establish the validity of **correlations of burner performance with spray operating conditions** (with a strong emphasis on the atomization process itself). Major concerns in the development of hydrothermal oxidation (HTO) as a zero-emission treatment technology for aqueous wastes are unknown processing conditions and poorly understood "unit operations", specifically with respect to salt formation and deposition, metallic corrosion, and heat transfer in near-critical fluids. Addressing the measurement and data issues associated with these three technology barriers form the core of the Division's **research in HTO technology**. Development of *in situ* (optical) detection methods for monitoring corrosive species (reactants and products) at the temperatures and pressures characteristic of HTO is also very important to the electric power industry. Babcock and Wilcox, a major process engineering firm, is collaborating with us, under a Cooperative Research and Development Agreement (CRADA), to research a solution to this measurement problem.

In recent years, the Division's sensors thrust has grown to constitute almost 15% of our work. It is comprised of two major research efforts: **micro-machined gas sensor arrays** and **sensing applications of self-assembled monolayers (SAMs)**. The first effort is collaborative with the Semiconductor Electronics Division of the Electronics and Electrical Engineering Laboratory. The technology is based on CMOS-fabricated SiO_2 bridge structures formed with silicon micro-machining to make 'micro-hotplate' arrays. Chemical sensing capability is achieved by depositing metal oxides, e.g., SnO_2, and surface-dispersed catalytic metal-additives to form robust, electrical-conductance based sensing elements on the micro-hotplates. Because of their small mass the micro-hotplates can be heated to near 1000°C and cooled back to ambient temperature with time constants in the millisecond range. This enables temperature driven sensing (TDS), which exploits adsorption/desorption kinetics, to enhance the sensitivity, selectivity, and repeatability of the sensing response. Combined with selection of metal oxides and catalysts, TDS arrays offer excellent potential for real-time sensing of multi-component gas mixtures. In 1995, two patents were issued for the fabrication and application of these devices. To date, 26 companies have contacted us to discuss licensing this technology. The objectives of our effort are to develop the knowledge-base required to optimize multi-species detection and quantitative analysis and to resolve generic device-processing issues which could limit commercial application.

The self-assembly of monolayers of alkanethiols, of the general formula $X(CH_2)_nSH$, on the surfaces of gold substrates forms the basis of the sensing applications of SAMs program. These molecules attach via the thiolate headgroup to form strongly chemisorbed and densely packed assemblies with surfaces having terminal-group controlled functionality. The SAMs can be 2-dimensionally patterned providing variable length and terminal-group arrays for selective attachment and detection of biological and organic molecules. Our research seeks to develop the means to reliably produce the desired SAM arrays, including studies of the roles of chemical and structural "forces" in the self-assembly process, and to develop approaches to sensing and identifying attachment of analytes. SAM based sensors hold great promise for applications in medicine, pharmacology, and biotechnology.

Selected Program Highlights:

The Division has responsibility to provide and disseminate the International Temperature Scale of 1990 (ITS-90) over the range 0.65-1235 K. A major goal of NIST's **temperature standards program** (one shared by only a few national standards laboratories throughout the world) is to realize ITS-90, as defined, over this complete range. This year we extended our previous realization (1235-24.6 K) down to 13.8 K (the triple point of equilibrium H_2) and added the range 0.65-4.2 K (which is based on the vapor pressures of ^3He and ^4He). The only remaining gap in our realization relies on gas thermometry in the range 3-24.6 K and this is expected to be realized within the coming year. In practical process control applications, thermocouples (TCs) are the most widely employed of all thermometers. This year we completed an investigation leading to the development of **Pt/Pd TCs** as very accurate and stable TCs for high temperature applications. They have demonstrated remarkable (±20 mK) stability for temperatures in the range up to 1200 K. These devices will be increasingly important in semiconductor manufacturing which requires very accurate temperature control in wafer processing furnaces. In the coming year, the thermal EMFs of these new TCs will be determined against ITS-90 in a project joint with the national standards laboratory (IMGC) of Italy. This year we initiated a competence project, joint with the Thermophysics Division and the Radiometric Physics Division of the Physics Laboratory, to improve (by factors of 3 to 8) the accuracy of **thermodynamic temperature measurements** in the range above 500 K. We will extend high accuracy acoustic thermometry from nominally 373 K to the 933 K (the Al-point). The Radiometric Physics Division will link to our measurements at the Zn- (693 K) and Al-points and then extend to the Au-point with an accuracy goal of 10 mK.

A great many new projects were initiated in FY95 in the general area of fluid transfer standards. Construction of a major new **calibration and testing facility for gas flowmeters for vehicle exhausts** was started this year in our flow standards project. This facility, developed in response to the needs expressed to NIST by the American Industry/Government Emissions Research (AIGER) consortium, will provide gas compositions simulating those of automotive exhausts. The combination of high moisture content and high temperatures (to 700 K) are the most significant characteristics of this measurement problem. Calibrations are required in the flow range of 1 to 36 standard liters per second. The facility will be commissioned in FY96. Efforts to upgrade **NIST's hydrocarbon-liquid flow calibration facility** to achieve a four-fold reduction in uncertainty to ±0.025% were also initiated in FY95. Research to develop a **new liquid volume calibration facility** with a four-fold improvement in uncertainty down to ±0.01% was completed in FY95 with joint sponsorship by the American Petroleum Institute. A new calibration facility was designed and ordered with installation and commissioning expected in early FY96. A new instrument to enable **liquid density measurements** at the level of 30 ppm was commissioned this year. Based on hydrostatic weighing of a Si-crystal standard, this system will be used to certify new SRM liquid density standards early in FY96. An **air speed proficiency testing program**, with instrument manufacturers participating under a CRADA, was formed in FY95 with the goal of improving the performance of air speed calibration facilities via round robin testing. Currently, we have eight participants in the program and expect to complete the first round of testing and evaluation in the coming year. Finally, we initiated

a new program with the Electric Power Research Institute to investigate the use of **non-intrusive acoustic flowmeter technology** for improved accuracy in measurements of cooling-water flows in power plants.

The most significant development in the humidity measurements area in this past year was the initiation of a project, joint with the Thermophysics Division, to use **cavity-ring-down-spectroscopy to measure low-level water in gases**. This novel technique measures the change in energy of a laser pulse (propagating in a very high reflectivity spherical mirror cavity) arising from optical absorption by the gas. The research this year produced a method to correct ring-down signals for multi-mode lasers and demonstrated quantitative measurements of a weak O_2 absorption These results hold promise for parts per billion sensitivities for water vapor measurements. This work was part of the Division's program in support of new measurement technology for semiconductor manufacturing. Another highlight in this program was the demonstration of the use of **planar laser-induced fluorescence to provide 2-dimensional maps of the concentration** of metastably excited Ar and the CF_2-radical in our reference plasma reactor, the **Gaseous Electronics Conference (GEC) cell**. This year we also completed development of an **electrical equivalent-circuit model for a capacitively coupled plasma reactor**, e.g., the GEC cell. This model relates externally measured currents and voltages to plasma properties important in etching, for example, electron densities, ion currents, and sheath widths. Combinations of these two measurement techniques will be used in the coming year for benchmarking a 2-dimensional plasma model and the supporting chemical mechanisms. In a related effort, we have completed development and publication of an extensive **chemical kinetic mechanism for high temperature fluorocarbon chemistry** which will find application in the areas of plasma etching and polymer formation, as well as in fire suppression, incineration, and atmospheric chemistry. The development of this mechanism relies heavily on the use of **computational chemistry**, a tool which is of great value for quantitative estimation of important reaction intermediates and rates throughout our materials chemistry and semiconductor models and data programs. As part of these programs, we developed and published a **solution to the time dependent "master equation"**, the set of coupled equations which describe the time dependence of chemical species concentrations (including internal energy distributions) during a chemical reaction. This solution is now being implemented in a new computer tool, with supporting user interface, to allow greatly improved prediction of chemical reaction rates, including, for the first time, chemically-activated and isomerization processes. Chemical mechanisms are vital inputs required for accurate process models. The latter add coupling to mass and energy transport equations, and often must include multiphase, e.g., gas-solid, reaction steps. Developments of this type are the goal of a project to couple particle generation and transport with fluid flow and chemistry to **model deposition and particle contamination in a spinning-disk thermal CVD reactor**. This system, currently under construction will serve as our reference reactor for thermal CVD processing used by the semiconductor industry.

Modification, design and construction is a large portion of the effort in the spray combustion program in FY95 and FY96. This work involves enclosure of the spray burner to allow emission measurements and designing, selecting, installing, and testing an array of on-line chemical and soot measurement systems which will run in parallel with the spray characterization facilities. **Atomizer designs**, for example an acoustically driven system developed by Fluid Jet Associates (a CRADA partner) and a steam-assisted atomizer for use with variable composition waste fuels, will be tested in this program. In the HTO program, we have demonstrated the first ***in situ* observation of corrosion** spinels, mixed metal oxides resulting from the oxidative corrosion of stainless steel, in near-critical and supercritical water conditions using Raman spectroscopy. In this work, the species observed in the *in situ* studies were different from those observed in post-exposure analyses outside the water environment. This result suggests a route to more complete understanding of the corrosion mechanism which will be explored in a collaborative project with researchers at the Massachusetts Institute of Technology (MIT) in the coming year. In another continuing collaboration

with MIT, we designed and demonstrated use of a special optical cell to study the process of **salt deposition near the water critical point**. In a study of the destruction of refractory intermediates by HTO, we have demonstrated **ammonia destruction of over 90% by using hydrogen peroxide** instead of O_2 which had yielded only 50% destruction levels. This observation suggests a fundamentally different chemistry for H_2O_2 in contrast to the usual assumption that it simply serves as a convenient source of molecular oxygen.

The central focus in the micromachined gas-sensor arrays program this year has been on device fabrication issues. The ability to produce multi-element arrays routinely and reliably limits our efforts to develop methods for optimization of sensing oxides and catalytic overlayers and for developing optimized signal processing approaches. Currently aluminum is used in all micro-hotplate metal layers., i.e., forming the thermometer plate and the 4 electrical leads for the sensing film. Aluminum sensing-film contact surfaces, exposed to etchants in both the final CMOS processing steps and in the micro-machining process, are severely degraded, resulting in poor electrical contact with sensing films. This year's effort has examined a wide variety of possible solutions to the Al-contact problem, such as alternate micromachining etchants, application of various buffer layers to improve electrical contacts, the use of laser deposited metals for contact repair, and the design of a chip structure based on tungsten metallization. Each has had limited success, but as yet no single approach has been found that provides reliable contacts and requires minimal, or no, post processing steps. A major thrust in the coming year will be to obtain a solution for this difficulty. A major success in the processing area this year was the demonstration of "self-aligned" thin film deposition of sensing oxides and catalytic metal surface additives on a multi-element array. Self-aligning depends principally on control of the temperature of each individual sensor pixel.

Spatially patterned, immobilization of active DNA probes was demonstrated in the sensing applications of SAMs program this year. Single-stranded DNA probes (cytosine-C_{25}) were attached to Au substrates via a thiol head group. Mercaptohexanol was used as an inert diluent to limit nonspecific adsorption of target DNA. Patterning was accomplished by ion bombardment to remove the SAM from micrometer-size regions of the surface. A second SAM, consisting of a thiol derivatized T_{25} (thymine) probe diluted in mercaptohexanol, was then selectively adsorbed on the surface. This deposition was found to occur only in those regions that had been ion etched. Subsequent exposure of the patterned SAM to A_{25} (adenine) resulted in hybridization localized to the T_{25} regions. This approach, using self-assembly of mixtures of thiol-derivatized probes and alkanethiols on gold surfaces, holds great promise for improving our understanding of DNA-probe modified surfaces and for the design of sequence-specific sensors.

Organizational Structure:

In FY95 the Division was organized into five Groups: Fluid Flow, High Temperature Processes, Reacting Flows, Process Sensing, and Thermometry. The following pages present more detailed discussions of the accomplishments and some plans for the coming year in each of the Division's programs.

B. Selected Technical Reports

1. Calibration and Test Services Provided by the Process Measurements Division

G.J. Rosasco, V. Bean, B.W. Mangum, G.E. Mattingly, and J.R. Whetstone

Objective: To maintain national standards according to the definitions of the relevant units, and to disseminate the NIST-realized units to industrial users and government laboratories (DoD, NASA and state) that require calibrations against and direct traceability to national standards.

Problem: The Process Measurements Division is responsible for realizing, maintaining, and disseminating the national standards for measurement of temperature (in the range 0.65-1235 K), humidity, fluid flowrate, liquid volume and density, and air speed. Issues of primary importance in this area involve assessing and meeting, to the extent practicable, customer requirements for accuracy in their measurements, improving the efficiency of calibration services, developing methods to enable appropriate realization of standards in the customer's laboratories, and serving as the primary resource supporting the national measurement system.

Approach: Provision of customer-appropriate access to national standards of measurement involves a range of activities: maintenance and improvement of primary standards, participation and leadership in U.S. and international standards committees, performance of instrument calibrations and tests, operation of Measurement Assurance Programs, proficiency and round-robin tests, development of mechanisms for realization of secondary standards in customer laboratories, and a wide range of consultation and customer assistance services. The calibration and test services provided by the division are described in *NIST SP 250, NIST Calibration Services Users Guide*, and its supplements.

Results and Future Plans: Our capabilities, experimental techniques and the facilities used to perform these services are being upgraded, with concomitant improvements in efficiency and in measurement uncertainties. Activities in the thermometry area during FY95 included the construction, evaluation and use of new Zn, Al and Ag freezing-point cells in TC calibrations, and the completion of the automation of the calibrations of industrial platinum resistance thermometers, thermistor thermometers, and thermocouples in the Liquid-in-Glass Calibration Laboratory. Automation of the calibrations in this laboratory will be completed in the coming year with the inclusion of the calibration of liquid-in-glass thermometers.

In the area of humidity measurements, we continue the construction of a new gravimetric hygrometer in an effort to re-establish and extend our primary moisture measurement capability. This instrument, based on state-of-the-art refinements of traditional gravimetric humidity measurement approaches, will enable 0.1% uncertainty measurements in the range from +40 °C to approximately −42 °C frost point (100 ppm_v). This system also will serve as a reference for our newest instrumental developments which seek to establish a new primary standard for humidity measurements based on optical absorption. All subsystems of the new gravimetric device have been constructed and made operational, with only the mass measurement system needing some final refinements to meet design goals; the entire system is expected to be operational by the end of FY96. A new low-frost-point humidity generator, designed to provide very low moisture concentrations, with frost points to −100 °C (10 ppb_v), also is under construction. These ultra-low-moisture-content standards are required to calibrate measurement instrumentation used to assure contaminant-free process gases in the semiconductor industry. This system uses all metal seals to assure very high gas purity and employs heat pump and thermoelectric cooling technology, thereby eliminating potentially harmful and expensive refrigerants. All subsystems for this new generator also have been constructed and tested. Temperature measurement and control techniques are being refined to assure achievement of the required millikelvin temperature stability and uniformity. The system is expected to be operational in FY96.

Calibrations and Special Tests Performed by the Process Measurements Division		
Service	Number of Items	
	total	for industry
Standard Platinum Resistance Thermometers (SPRTs)	82	50
Thermocouples (TCs)	163	159
Laboratory Thermometers (includes 178 LIG, 28 IPRTs, 69 thermistors)	275	196
Special Tests for NIST CIFP	74	
MAP in SPRTs	2	
Fluid Flow Meters	31	27
On-site HC Liquid Flow Tests	2	2
Volumetric Test Measures	75	75
Air speed Instruments	28	21
Reference Standard Hydrometers	40	30
Humidity Measurement Instruments	26	16

In the area of international intercomparisons, NIST is chairing an eleven nation effort under the auspices of the Consultative Committee on Thermometry of the CIPM covering Europe, North America, and Asia which involves use of an optical hygrometer to compare realizations of humidity standards from −70 °C to +40 °C dew point temperatures. In the one comparison completed this year between NIST and the European Union, we obtained agreement within the stated uncertainties of the participants, i.e., better than 0.1%. We also have initiated a second intercomparison of humidity generators with participants from the semiconductor industry under the auspices of Semiconductor Instruments and Materials International (SEMI).

New efforts in the area of standards for fluid transfer, involving liquid density and volume standards and a new simulated vehicle-exhaust gas flow calibration facility, are discussed in the reports following. Other efforts this year involve the upgrading of our hydrocarbon flow calibration facility to achieve uncertainties of 0.025%. This calibration service, which provides support vitally important to US jet engine manufacturers for their testing activities, and to DoD engine performance testing facilities, is based on a passive-piston volumetric device originally purchased by the US Navy. This year's effort focussed on making all subsystems operational, upgrading electronics and software components and replacing all malfunctioning flow control hardware. The system is expected to be fully operational in FY96. An interlaboratory intercomparison test of gas flow measurement capabilities has been done with NRLM (Japan) and results have been helpful in guiding Japanese efforts to improve their temperature measurement systems in their new gas flow facility. An extensive interlaboratory comparison was completed with the water flow measurement group of the Naval Ship Systems Engineering Station (NAVSSES) in Philadelphia. In the area of air speed measurements, a new proficiency testing program involving round robin testing with meter manufacturers and secondary calibration laboratories has been organized this year as an Air Speed Proficiency Testing CRADA. The goal of this program is to establish traceability to the NIST primary standard in all the participating

laboratories. It is also expected that this effort will provide the basis for a new international intercomparison of air speed measurement standards.

Publications:

Mangum, B.W., "**Reproducibility of the Temperature of the Ice Point in Routine Measurements**," NIST Technical Note 1411, U.S. Government Printing Office, Washington, DC 20402, 24 (1995).

Ripple, D. and Young, S., "**NIST ITS-90 Thermocouple Database, Version 1.0**," NIST Standard Reference Database 60, U.S. Government Printing Office, Washington, DC 20402 (1995).

Strouse, G.F., "**NIST Measurement Assurance Program for the ITS-90**," Proceedings of the Naval Test and Calibration Symposium, Arlington, VA (1994).

2. *Implementation and Dissemination of the International Temperature Scale of 1990*

***B.W. Mangum**, C.W. Meyer, W.L. Tew, G.F. Strouse, G.W. Burns, D.C. Ripple, A. Ince (UME, the Turkish National Metrology Institute, Gebze-Kocaeli, Turkey), Y. Liu (NIM, National Institute of Metrology, Beijing, China), C.D. Vaughn, and G.T. Furukawa (Guest Researcher).*

Objective: To realize the ITS-90 as it is defined over the range from 0.65 K to 1235 K, to investigate the non-uniqueness of the ITS-90 over this temperature range, to intercompare our realization of the ITS-90 with those of the national standards laboratories of other countries, and to disseminate the scale to the user community.

Problem: The ITS-90 extends upward from 0.65 K. The realization of this scale, as it is defined, has been completed at NIST over the range from 83.8058 K to 1234.93 K. The realization of the ITS-90 over the range from 0.65 K to 83.8 K, however, has not yet been completed at NIST. Consequently, NIST still uses a "wire scale", based on some old NBS work and on some thermometers calibrated by NPL, as the NIST reference for calibrations in the region 0.65 K to 83.8 K. This wire scale consists of an SPRT-based scale spanning the region 13.8 K to 83.8 K and used primarily for calibration of SPRTs, and a rhodium iron resistance thermometer (RIRT) based scale spanning the region 0.65 K to 27.1 K and used primarily for calibration of RIRTs and germanium resistance thermometers. Recent measurements at NIST indicate that the wire scale may be in error by about 1 mK in certain regions of the scale below 25 K. Realization of the ITS-90 below 83.8 K, as it is defined, will free us from the wire scale, and this will reduce our uncertainty of calibrations in that range. There are other uncertainties resulting from the non-uniqueness of the scale over the range from 1.25 K to 1243.93 K that have not yet been evaluated. The magnitudes of these non-uniquenesses must be determined in order to arrive at the total uncertainties of realization and dissemination of the scale. Also, new and/or better methods for dissemination of the ITS-90 (apart

from calibration of thermometers) are needed to get the scale to users requiring high accuracy.

Approach: The completion of the implementation of the ITS-90 will be accomplished through the realizations of the temperature of the triple-points of Ar (83.8058 K), O_2 (54.3584 K), Ne (24.5561 K) and e-H_2 (13.8033 K) in large non-transportable cells and in transportable cells suitable for use in international intercomparisons, through measurements of the saturated vapor pressures of ^{3}He (0.65 K to 3.2 K), ^{4}He (1.25 K to 5.0 K) and H_2 [at (17.035±0.010) K and at (20.270±0.010) K], and through interpolating constant-volume gas thermometry (ICVGT) (3.0 K to 24.5561 K), using ^{3}He or ^{4}He gas as the working fluid. To achieve an inaccuracy in temperature of ≤0.1 mK, the pressure must be measured with an inaccuracy of <30 ppm (for vapor pressures) and with an imprecision of <3 ppm (for gas thermometry). The gas pressures are measured with a gas-lubricated piston gage in series with a differential capacitance diaphragm gage. The non-uniqueness of the ITS-90 will be determined by investigating its different sources in the various temperature ranges and determining its magnitude over those different ranges. In some cases, e. g., for the range from 933 K to 1235 K, a large number of thermometers are required for this investigation. Consequently, collaborations with national laboratories of other countries are desirable, or necessary, in order to have enough thermometers for a meaningful investigation. The ITS-90 is disseminated through the calibration of thermometers, SRM fixed-point cells of pure materials, SRMs of pure metals of the defining fixed-point materials, and SRM thermometers.

Results and Future Plans: The He and H_2 vapor-pressure ranges of the ITS-90 and the seven fixed points used in defining the scale between 0.65 K and 83.8058 K were realized in our low-temperature scale-realization facility, and the scale in that range and at those fixed points was retained on two SPRTs and/or three RIRTs, depending on the temperature range. The temperatures from vapor-pressure realizations differed from temperatures on our wire scale by as much as 0.8 mK, outside the expected agreement. The non-uniqueness of the ITS-90 in the range 1.25 K to 3.2 K (the region of overlap of ^{3}He and ^{4}He vapor-pressure ranges) was investigated. The results showed a non-uniqueness of about 0.2 mK over the range. The realization of the ITS-90 by ICVGT between 3 K and 24.6 K will be performed in FY96, and the non-uniqueness of the scale over this range will be determined.

Construction of a high-purity gas-handling system for preparing sealed, transportable triple-point cells to be used for realizing the fixed points of the ITS-90 at temperatures between 13.8 K and 84 K (and some secondary points at intermediate and higher temperatures) was completed. Some triple-point cells of e-H_2, Ne, O_2 and Ar will be constructed and evaluated during FY96. The cells will be used in calibration of thermometers by the fixed-point method and also used in international intercomparisons to ascertain the agreement of our realization of the ITS-90 fixed points with those of other nation's standards laboratories. Such intercomparisons are the basis for bilateral agreements between the USA and other countries on the equivalence of our respective realizations of the scale.

The triple point of water is the reference point of the thermodynamic temperature scale and of the ITS-90 and its temperature determines the size of the unit of temperature. Thus, we continue our effort to ascertain how closely our realization of the triple point of water agrees with those of other nations (and from cells of different manufacturers). This year we compared our cells with two cells constructed at NIM, two cells constructed at UME, and with three cells of a round robin organized by the BIPM under the aegis of the CCT and involving cells of various constructions from KRISS (Korea), IMGC (Italy), and VNIIM (Russia). To within our reproducibility of 0.02 mK, the NIST reference cells were determined to be of equal or superior quality.

Efforts to determine the non-uniqueness of the ITS-90 in the ranges 933 K to 1235 K and 273 K to 933 K were continued this year. These data are required to establish realistic uncertainty statements for calibrations. Since a large sample of (HT)SPRTs is required for this study and since our supply of (HT)SPRTs is inadequate for the range 933 K to 1235 K, we organized a collaborative

effort with the national laboratories of Italy (IMGC) and the Netherlands (VSL). (HT)SPRTs for investigation, selected on the basis of their stability upon high-temperature exposure, have been calibrated from 273 K to 1235 K and are undergoing comparison measurements in our high-temperature comparator, for which alterations and evaluations for optimal performance were completed. When the intercomparisons at NIST and at IMGC of our respective (HT)SPRTs are completed in FY96, the (HT)SPRTs will be exchanged between NIST and IMGC and then new data on the exchanged (HT)SPRTs will be obtained by the respective institutions.

In recent years, we have had a significant effort in developing fixed-point cells with the goal of disseminating the ITS-90 to secondary calibration laboratories. In this effort, four freezing-point cells containing 99.9999+% pure Sn and four freezing-point cells containing 99.9999+% pure Zn were constructed and their melting/freezing behavior was evaluated as part of the certification process of the cells for use as new Standard Reference Materials (SRMs) 1747 (Sn freezing-point cell) and 1748 (Zn freezing-point cell), all for use in calibrating (HT)SPRTs. The freezing-point temperatures of the Sn cells (505.078 K) and the Zn cells (692.677 K) were highly reproducible and agreed to within 0.2 mK and 0.5 mK, respectively, with our reference cells. Other features of the melting/freezing curves also indicated the Sn and Zn samples to be of extremely high purity. SRMs 1747 and 1748 are now available for purchase.

Another method of disseminating the ITS-90 to secondary calibration laboratories and others requiring high accuracy is through highly stable thermometers that require infrequent or no re-calibration. In this regard, we initiated a project to produce 20 Au/Pt thermocouples (TCs) as SRM 1749. This SRM will be completed in FY96 and the TCs will not require recalibration.

Publications:

Strouse, G.F., **"Standard Reference Material 1744: Aluminum Freezing-Point Standard,"** NIST SP 260-124, Government Printing Office, Washington, DC, 24 (1995).

3. High-Temperature Thermocouple Research and Sensor Development

***G.W. Burns**, D.C. Ripple, K.G. Kreider, B.W. Mangum, C.T. Avedisian (Cornell Univ.), and D. Wallace (Microfab, Inc.)*

Objective: To develop new sensors (e.g., wire and/or thin-film thermocouples) as reference thermometers for secondary calibration laboratories and/or as fairly inexpensive, high-accuracy, high-stability, high-temperature thermometers for industrial use, including use in surface-temperature measurements.

Problem: The problems being addressed are two-fold: (1) the lack of stable thermocouples (TCs) to serve as reference standards in secondary calibration laboratories and/or as high quality thermometers for industrial applications. TCs currently used as reference standards (types S, R and B, all of which contain Rh), and as the best available thermometers for most industrial applications, have, at best, at the time of calibration, uncertainties of about 0.1 K at the Au freezing point (1337 K). These uncertainties increase rapidly with increase in temperature above 1337 K to about 1.6 K at 1725 K. Also, due to unstable inhomogeneities and selective oxidation of Rh, the emfs of these TCs drift with use, becoming much more uncertain, perhaps an increase in error by as much as a factor of 10 at 1337 K. (2) Unreliable measurements of surface temperatures caused by use of traditional contact thermometers or non-contact radiation thermometers, e. g., in the semiconductor industry. Accurate high-speed measurements of temperatures of surfaces are especially critical in semiconductor wafer preparation by rapid thermal processing (RTP) because accurate control of temperature during short, high temperature exposures, is critical to product quality and device performance.

Approach: To address the need for stable TCs to serve as reference standards in secondary calibration laboratories and/or as high-quality thermometers for industrial applications, TCs of pure noble metals, such as Au, Pt and Pd, are being investigated. These metals can be produced at exceptionally high purity (5-6 nines) and are

generally resistant to oxidation in high temperature environments. Since the TCs are constructed of these pure metals, inhomogeneities are small, defects can be essentially removed by annealing, and the TCs are stable. To address the need for accurate measurements of temperatures of surfaces, the feasibility of thin-film TCs is being investigated. These devices become part of the surface and thereby obviate the uncertainties associated with conventional contact thermometers (uncertainty of the quantitative relationship of the measured temperature and the surface temperature) and with radiation thermometers (uncertainty with respect to the time-dependent, effective emissivity of the surface).

Results and Future Plans: In our efforts to develop stable, high-accuracy TCs, Au/Pt TCs have been found to be an excellent choice for temperatures up to 1275 K (stability of a few mK). We have developed a reference function for them and are producing the Au/Pt thermocouples as SRM 1749. The work on that SRM will be completed in FY96. In an effort to develop a TC for use to about 1675 K, the stability of Pt/Pd TCs as a function of annealing procedures has been investigated up to 1475 K; some have been heat treated at 1375 K for more than 1000 h and stabilities of 5 mK to 10 mK per 100 h at 1375 K were obtained. Also, inhomogeneities equivalent to only 4 mK to 16 mK were observed. Six such Pt/Pd TCs were constructed and evaluated for use in a collaborative project (NIST and IMGC) to determine their reference function up to about 1675 K. This function is necessary to facilitate the use of these TCs as a high-temperature transfer standard and in industrial applications. The evaluation of these TCs up to 1675 K will be completed in FY96 and their reference function developed in early FY97. The temperatures of the emf-t_{90} experiments required to develop the reference function will be measured between 273 K and 725 K with SPRTs, between 725 K and 1275 K with Au/Pt TCs, and between 1275 K and 1675 K with radiation thermometers.

New techniques for preparation of thin-film TC arrays for accurate temperature measurements, with high spatial resolution (a few micrometers) and short response times (of the order of a millisecond) were investigated this year. Such device capabilities are important in RTP and for droplet impingement studies. A photolithographic technique based on lift-off (a technology widely used in semiconductor fabrication) was adapted for producing Cu and CuNi alloy TCs (familiar copper-constantan TCs), 0.10 μm thick by 30 μm wide on alumina substrates. Several test coupons containing an array of 20 such TCs were produced for studies of solder droplet quenching in a collaborative effort with Microfab, Inc.. The thermal history of the solidification of small droplets is important to the development of their new technology for "printed" circuit board fabrication. Also, in a collaboration with Cornell University, we demonstrated droplet temperature measurements with submillisecond resolution. In these initial studies of rapid solidification of small droplets of water, butanol, and ethanol, we were able to observe the freezing plateaus of the different substances. We also completed fabrication and assembly of a thin-film TC test cell suitable for calibration and stability testing of the TCs from 273 K to 1275 K.

In FY96, investigations will begin on the stability of thin-film TCs using the new calibration cell and on the use of thin-film TC techniques to provide more accurate measurements of temperatures of surfaces of Si wafers in RTP environments. In addition, we will develop the materials technology of fabricating thin-film TCs on alumina and oxidized Si wafers. noble metals are required for high temperature operation; however, adhesion is a problem that must be solved to allow device fabrication with these metals.

4. *Thermodynamic Temperature Measurements*

***D.C. Ripple**, B.W. Mangum, K. Gillis (838), and M. Moldover (838)*

Objective: To improve the accuracy of thermodynamic temperature measurements above 500 K by a factor of 3 to 8.

Problem: There remain unresolved inconsistencies in previous measurements of thermodynamic temperatures at 500 K and above by two groups of researchers at NIST (each group used a different gas-thermometry apparatus). Those inconsistencies led to unnecessarily large uncertainties in the thermodynamic values assigned to the defining fixed points of the ITS-90 and, hence, to all temperatures measured on the ITS-90 by radiation techniques, for which reference is made to either the freezing-point temperature of Ag, Au or Cu.

Approach: Thermodynamic temperatures between 500 K and 933 K will be measured by acoustic techniques, using spherical resonators. Acoustic thermometry relies on the relationship of the speed of sound in an ideal gas to the thermodynamic temperature. Speed of sound measurement via spherical resonator techniques, previously applied to the high accuracy determination of the Boltzmann constant, will be extended to high temperature operation. Gas purity also will be controlled to a very high degree, a major challenge in this high temperature environment. We expect reductions in the uncertainty of the thermodynamic temperature of various high temperature fixed points by factors of 3 to 8. The goal for the Au-point is a reduction of a factor of 5 to an uncertainty of 10 mK. The results will have application to radiometric measurements of temperature to much higher temperatures (upwards to maximum measured temperatures of about 4000 K) since the new, more accurate values of the thermodynamic temperatures will be the basis for the radiometric measurements.

Results and Future Plans: This project to improve the accuracy of thermodynamic temperature measurements above 500 K was started in FY95. The focus for this year has been on planning. A system for continual purging of the resonator with high-purity gas with sub-ppm pressure oscillations was developed. This purging is required in order to remove any contamination of the working high-purity gas. Also, a conceptual design of a low-gradient furnace for the resonators was completed and experiments on resonator seals and materials were begun.

In FY96, an acoustic resonator suitable for operation at 725 K will be constructed, as will the resonator's related gas handling and temperature control systems.

5. *Fluid Mechanics and Flow Metering Research*

G.E. Mattingly, T.T. Yeh, P.I. Espina, J.D. Wright, and J.M. Allingham

Objective: To investigate and expand the capabilities of Computational Fluid Dynamics (CFD) and ultrasonic flow measurement technology and assess their potential for improving flow measurements in "non-ideal" meter installation conditions which can lead to significant flow metering errors.

Problem: Flow meters can be very inaccurate when the velocity profile entering the meter is not the "fully-developed", equilibrated distribution of flow that is produced by "ideal" conditions of long, straight lengths of constant diameter pipe preceding the meter. However, because of space restrictions and process piping requirements industrial meter installation designs cannot usually arrange "ideal" conditions. These situations can produce significant errors in material accountability. To remedy these situations, *in situ* calibrations or calibrations in duplicate piping are currently the only alternatives, but these are seldom feasible. This is particularly true in the electric power generation industry where large diameter, high flowrate water measurements are critical to plant control and rating-derating decisions. For this reason, the Electric Power Research Institute (EPRI) has requested NIST assistance in evaluating ultrasonic flow metering technology in a cost-shared program designed to produce guidelines and standards to improve flow measurements. Concerns for improved standards and guidelines of this type have long been the focus of our research in the Flow Meter Installation Effects (FMIE) consortium.

Approach: The non-ideal flow distributions arising from commonly employed piping arrangements, e.g., elbows, reducers, headers, etc., have been measured as part of our FMIE research effort for a number of years. The FMIE work included measurement of meter performance (typically for orifice and turbine meters) in the non-ideal flows and correlation to flow characteristics such as swirl and skewness. In the last few years, we have started an investigation of the use of computational fluid dynamics (CFD) to model these flows and shown, for example, that CFD descriptions of the flow through a conventional pipe elbow agreed favorably with the corresponding LDV measurements. Thus, CFD may afford a reliable method (which can be validated from our FMIE database) for description of the complete flow distributions for a wide variety of industrially important piping geometries. Unfortunately, most conventional flowmeters are far too complex to model accurately the effects of non-ideal flow distributions on meter performance. In contrast, ultrasonic flowmetering technology is based on measurement of the time-of-transit of a sound pulse along a given path through the moving fluid. Knowledge of the flow distribution should enable calculation of the meter response, and it is also possible that measurements along multiple paths could, in conjunction with modeling, yield information about flow distributions inside the pipe. This, in effect, affords the potential for *in situ* diagnostics of non-ideal installations of great interest to the FMIE consortium. In addition, ultrasonic techniques are of special interest to EPRI because the technology is simple, non-intrusive, and can be installed easily by clamping sensors on the outside of the pipe.

Results and Future Plans: In the past year, we completed our FMIE effort to measure the flows in the outlet piping from a generic header configuration and reported these results to the consortium membership at the annual meeting of this group. During this meeting we changed the central research strategy of this program from one which used only LDV to one which used mainly CFD with limited LDV results as needed for validation. We made this change based on the success of a project to assess the potential of commercially available CFD codes to model non-ideal turbulent pipe flows and to produce more complete descriptions of these flow fields. Since our earlier LDV efforts measured the flows at specific downstream positions from selected piping configurations, we could only interpolate or extrapolate to try to understand flow phenomena at other locations. With CFD results, we obtain a more complete picture of the whole flow field into, through, and out of pipe elements and we can

evaluate these by comparisons to previous LDV measurements of the exiting flows. This alignment of our previous FMIE program and our CFD assessments with the objectives of the NIST-EPRI project is expected to benefit both efforts.

To prepare for the planned NIST-EPRI program we have designed an ultrasonic flow meter testing program that should produce the database needed to initiate the assessment of ultrasonic flow measurement. Additionally, we have profiled pipe flows in our 250mm diameter meter water flow test section and have added flow conditioning elements to attain ideal conditions for Reynolds numbers up to $3x10^6$. Our test plan will include arranging a conventional, long radius elbow and a concentric reducer upstream of our test section so metering performance in these non-ideal installations can be quantified for the same flow rates as tested in the ideal installations.

Our plans are to test clamp-on type, time-of-travel ultrasonic flow meters that are provided for this program by manufacturers. Invitation letters are being sent to prospective test participants. Meter test results for both ideal and non-ideal installation conditions are expected in FY96.

Publications:

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Yeh, T.T. and Mattingly, G.E., "**Flow Meter Installation Effects Due to a Generic Header**," NIST Technical Note (in press).

6. Volume Standards

V.E. Bean, *W.G. Cleveland, Jr., and J.F. Houser*

Objective: To provide improved calibration services for volume test measures up to 100 US gallons within an uncertainty of 0.01%.

Problem: To meets its goals of improved measurements in the field, the American Petroleum Institute (API) has requested NIST to reduce its quoted uncertainty for the calibration of volume test measures by a factor of four, down to 0.01%. Volume test measures are used to calibrate instrumentation for determining the flow rate in oil pipelines and the economics of custody transfer is the driving issue.

Approach: NIST is constructing a new primary standard facility for liquid volume measurements. Volumes will be determined by weighing the distilled water required to fill a test measure up to the reference mark, measuring the water temperature, and calculating the volume from the density equation for water. The technique will determine contained volumes and will establish limits for errors due to transfer. This gravimetric method is an improvement over current practice of calibrating volumes by transfer from NIST volume test measures which were calibrated gravimetrically. The new liquid volume primary standard facility is a cost-shared project with API. The laboratory space for this facility is required to have high levels of temperature uniformity and stability.

Results and Future Plans: The weighing systems need to be isolated from the air currents necessary to maintain the temperature requirements. The laboratory module to provide the necessary controlled environment is under construction. All of the balances and other instrumentation for the facility have been purchased and characterized. Preliminary results indicate that the accuracy goals are attainable but that temperature stratification in the water in the test measures is an issue that needs to be addressed.

The facility has been designed to accommodate future extension of the range to 500 US gallons, as requested by API.

7. Liquid Density Standards

V.E. Bean, W.G. Cleveland, J.F. Houser, and R.M. Schoonover (MEL)

Objective: To provide state-of-the-art liquid density measurement services.

Problem: Sensitive liquid density measuring instruments are now commercially available which use comparative techniques that require high accuracy reference liquids in order to achieve design performance. The supply of these reference liquids, formerly available from NIST's Standard Reference Materials Program, has been depleted. The facility that provided the NIST measurements for liquid density in the past is no longer available. In addition, the improvements in fluid flow rate metrology now under development at NIST require increased accuracy in density measurements.

Approach: NIST has developed a new primary standard for liquid density based on hydrostatic weighing of single crystal silicon in the liquid of interest. The density of the silicon crystal is directly traceable to mass measurements and dimensional measurements. The sample liquid whose density is to be measured is contained in a specialized weighing system where the temperature control requirements can be assured.

Earlier liquid density measurement capabilities at NIST were based on picnometry. Hydrostatic weighing of silicon has two advantages over picnometry. The first is that hydrostatic weighing is a primary standard. A picnometer is a comparator of the density of one fluid to that of another, and secondly, the uncertainty of the measurements with the hydrostatic weighing system are much smaller than those possible with picnometry.

Results and Future Plans: The liquid density measurement facility was completed during FY95. Preliminary results indicate uncertainties on the order of 10 parts per million are possible. The facility will be used in the near future to determine the density of toluene and isooctane which have been requested to replenish NIST's supply of standard reference liquids for density. We plan to study the long-term stability of the density of ampouled samples of these liquids. This facility will also provide fluid density measurements in support of NIST fluid flow rate metrology.

8. Exhaust Meter Calibration Facility

J.D. Wright, *G.E. Mattingly, and P.I. Espina*

Objective: NIST will establish an Exhaust Meter Calibration Facility (EMCF) that generates a simulated car exhaust with flows known to 1% uncertainty. The EMCF will test the performance of exhaust flow meters under the demanding conditions of widely varying flow, temperature, and composition found during actual vehicle testing.

Problem: Automobile manufacturers are working to develop ultra-low emissions vehicles and in order to meet clean air requirements. Among the critical tools required to validate ultra-low emissions performance are flow meters to accurately measure the flow of exhaust. The American Industry / Government Emissions Research group (AIGER) requested a facility in which exhaust flow meters can be performance tested and calibrated. There is currently no facility available which can generate flows with accurately known (yet widely variable) composition and with the extreme range of temperature and flow found in vehicle exhaust. Also, the methodologies for extending calibrations made under easily attained conditions (say room temperature and dry air composition) to the extreme conditions of real meter applications have not been thoroughly validated.

Approach: The EMCF will test flow meters under the conditions seen in actual vehicle testing by 1) accurately mixing component gases to simulate vehicle exhaust, 2) varying the exhaust temperature between 290 and 700 K, and 3) measuring the combined flow to better than 1% uncertainty. The flow range for the simulated exhaust will be 1 to 36 standard liters per second (sls) while humidified air flows supported by the facility will range from 1 to 100 sls. Each of the component gas streams (nitrogen, carbon dioxide, and argon) will be metered with a bank of three critical flow nozzles sized to encompass the flow range. The nitrogen gas stream will be preheated and passed through a humidifier vessel to introduce the desired flow of water vapor, and the water flow will be measured using an optical hygrometer. The mixed gas stream will be heated to the set point temperature by a

large electric circulation heater before entering the meter under test. The facility will have a computer data acquisition and control system which will allow the automated collection of calibration data at predetermined set points of composition, temperature, and flow.

The completed facility will be a significant contribution to the study of the effects of gas composition and temperature on flow meter performance. It will allow tests of the validity of the extrapolation of meter calibration data (via the appropriate dimensionless quantities for the particular metering method) to extremes of composition and temperature that are beyond the capability of existing calibration facilities. The EMCF will also be available for flow meter manufacturers working to develop meters that are immune to changes in composition and temperature.

Results and Future Plans: In the past year, the EMCF design was completed, the necessary equipment was procured, and construction of the facility has begun. The specifications and design of the EMCF were developed with feedback from the future customers of the facility via the AIGER group. Sample versions of the designed gas delivery systems were constructed and tested. The argon nozzle bank was built and procedures for nozzle calibration, temperature control, and flow calculation were developed which obtain accuracies better than the 0.3% required by the uncertainty budget. A prototype version of the nozzle bank control and data acquisition program was completed. An existing laboratory space was cleared and the design of laboratory modifications for electric power, compressed air supply, and a high temperature exhaust system were completed.

Work on the EMCF continues, including assembly of the gas delivery systems, piping, heaters, wiring, data acquisition and control programming, tuning of control systems, and calibration of the critical flow nozzles and associated instrumentation. The EMCF will be available for customer calibrations in FY96.

9. *Synthesis and Characterization of Nanostructured Materials*

M.R. Zachariah, M. Aquino-Class, M.J. Carrier, D. DuFaux, B.K. McMillin, K. Steffens, E. Steel(837), R.D. Shull (MSEL), R. Axelbaum (Washington Univ.), E. Blaisten-Barojas (George Mason Univ.), R. Ziolo (Xerox Corp.)

Objective: Development of knowledge base for vapor-phase processing of bulk quantities of nanostructured materials:

1. Characterization and modeling of sodium/ metal-halide based flame chemistry for production of unagglomerated metals and ceramics.
2. Development of generic methods for vapor-phase production of nanocomposites.

Problem: Various theoretical and experimental results have shown that materials can demonstrate new and enhanced properties (mechanical, optical, electrical, etc.) when constructed from materials whose composition and size has been controlled on nanometer scales. However, methods to reliably grow such materials with tunable composition, size, and morphology are lacking. In addition, the knowledge base necessary to design and control the chemical/physical processes inherent in vapor-phase gas-solid transformations needs development.

Approach: Our approach has been to use methods for synthesis of nanostructured materials directly in particulate form, with a special emphasis on methods that have the potential to be extended to the production of materials on a bulk scale. The vapor-phase route has been pursued as potentially the most robust generic method to supply the basic requirements for cost effectiveness in manufacture and the resulting material property. Two synergistic approaches are pursued: 1) development and modeling of new prototype methods and chemistries for materials production and investigation of their performance, including the use of advanced *in situ* diagnostics for characterization, 2) development and application of molecular based models for prediction of nucleation and growth of nanoscale materials.

Results and Future Plans: This years activities include development of an aerosol dynamics model

for growth of nanocomposite particles. The model was specifically applied to the growth of a FeO_x/SiO_2 superparamagnetic nanocomposite previously synthesized by a flame process and characterized by planar laser induced fluorescence (PLIF) and Mie (elastic) scattering. The results support both the viability of this modeling approach as well as providing insight into some of the rate controlling processes occurring during growth of a nano-composite. Molecular dynamics simulation has also been used to understand intra-particle phase segregation, which has been used to explain the morphology seen in the FeO_x/SiO_2 nanocomposite. Work this year has also included activities in conjunction with Xerox in the formation of magnetic ferrites from a flame process.

The primary activity this year has been the implementation of a novel sodium-flame process for the production of non-oxide particles. The basic chemistry for the process involves the reaction of sodium vapor with metal halides ($Na + MCl_x \Rightarrow M + NaCl$), which results in the condensation of small metal clusters encapsulated in salt. The chemistry is highly generic and should be applicable to the synthesis of a wide class of materials (metals, intermetallics, ceramics). The potential strength of the process is not only its generic chemistry, but the fact that a by-product of the reaction, NaCl, serves as a coating to the particles, preventing agglomeration. Furthermore, the synthesis scheme can clearly be classified as "green" as no toxic by-products are involved. Most of the effort this year has been directed toward the chemical characterization of a counter flow diffusion reactor incorporating this chemistry for the $TiCl_4$ and BCl_3 systems. We have monitored the consumption of Na via planar laser induced fluorescence (PLIF) of Na_2, and the production of the particle phase by Mie scattering. A chemical model has been constructed and tested against the experimental result and shows good agreement. Basically the chemistry associated with the formation of Ti, B and TiB_2 is very fast (favoring the use of turbulent flow for practical application) and consistent with sequential abstraction of halogens, prior to nucleation. Temperature plays a vital role, in that low temperatures will result in both salt and metal co-nucleating, which leads to smaller metal particles.

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10. *Models and Data for Semiconductor Processing*

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Objective: Provide the necessary information and scientific infrastructure to enable the use of process models and process controllers that are grounded in fundamental chemical/physical laws, with an emphasis on:

1. *Ab initio* quantum chemistry and reaction-rate-theory derived thermochemical and kinetic data for silicon-based process chemistries.
2. Development of user-friendly data handling and estimation procedures and software tools.
3. Development of software for modeling flow, chemistry, and particle contamination in prototypical thermal CVD reactors.
4. Benchmarking of key data and models against experiments.

Problem: Reactor and process design are currently limited to empirical trial and error approaches which tend to converge to semi-optimized states very slowly. For an industry, such as the semiconductor industry, where changes occur rapidly, this implies that processes are not adequately investigated prior to final implementation. This results in not only more costly, possibly poorer quality products, but also processes which may not be environmentally optimized.

Approach: Process simulation has the potential to improve the design process, and therefore, make it both more effective and more likely to have an impact on the final process within the given time constraints. The potential of process simulation has been enabled by ever-increasing computational power which has evolved to the point that very sophisticated models can be constructed for a variety of complex semiconductor processing steps. However, increasing complexity of models implies greater need for accurate thermochemical and kinetic data, not now available. Our approach is to both use and develop methods for reliably generating, from first principles, thermochemical and kinetic data suitable for process modeling. In some cases, we develop user friendly tools that will aid an experienced process engineer in generating the data necessary for modeling as well as methods and tools for efficient post-processing of simulation results. Furthermore, procedures for handling, collating, and disseminating the information in an efficient and timely manner are an important component to the task. Finally, the reliability and utility of the information we generate is both a function of the inherent quality of the data (which must be verified) and the demonstration of its utility to the user community. The latter point requires that models of prototypical processes be developed for which benchmarking studies can conducted.

Results: This year we focused on the development of fundamental thermodynamic and kinetic data through the application of *ab initio* molecular orbital methods and reaction rate theory. Data has been generated on the thermochemistry of a large body of neutral fluoro-oxyhydrocarbon species (110 molecules). Such data has been compared with literature values where available and has shown excellent agreement to heats of formation (< 10 kJ/mol). These results were used as the basis for construction of a reaction mechanism for the high temperature chemistry of fluorocarbons, which relied heavily on the use of transition state quantum chemical calculation as well as reaction rate theory methods. The data have application to both plasma etching chemistries as well as combustion of the off gases from reactors. Data obtained with these methods has also been used to determine thermochemistry and kinetics for the silicon-oxy-hydride system important to the chemistry of SiO_2 film formation. Both sets of computed chemistries suggest that these methods have remarkable potential to change the character and scope of process modelling by enabling extremely rapid, relative to experiment, generation of large bodies of high quality data.

A new reaction-rate-theory computer program has been developed that solves the time dependent master equation and uses the RRKM formalism. The program enables the computation of rates for

any arbitrary combination of recombination, isomerization, chemical activation and decomposition reaction channels. We have been implementing this program in a user-friendly format that should allow researchers, not fully versed in the methodology, to use the software effectively. We have also developed a first version of a program that enables more effective handling of large reaction data sets. The software will allow one to rapidly screen large reaction rate and thermodynamic data sets for the data needed for a specific modeling task.

As part of our effort to benchmark certain chemistries, we have been making high temperature kinetic and mechanistic studies for tetraethoxysilane decomposition (TEOS). This is the primary precursor used in both thermal and plasma enhanced CVD growth of silicon dioxide films. Models, currently being developed elsewhere, require fundamental data on both the kinetics of TEOS decomposition as well as qualitative mechanistic information. Results to date have determined the thermal decomposition rate of TEOS and a likely mechanism for the overall chemistry and are consistent with our quantum chemical computations.

We have developed a model for a rotating disk CVD reactor that incorporates flow, chemistry, and aerosol formation and transport. The code is a modification of the Sandia SPIN code and will be used to develop a model for particle formation during CVD. The principal goal of this work is to assess the effects of changes in reactor operating conditions on the levels of wafer contamination, some of which we expect is formed via an aerosol route. The model will be tested against an experimental spinning disk reactor currently being built for us at MIT/Lincoln Laboratories. This reactor will be suitable for both industrially realistic film growth and simultaneous optical characterization for benchmarking our model. Also conducted this year were studies of wafer contamination during processing in barrel-type CVD reactors. This involved development of a model for the transport of micron-sized particles which indicated that such reactors may be susceptible to the formation of particle attractors near the wafer surface. These attractors entrain particles of a certain size and hold them stationary in the flow. A novel treatment of the flow has involved the use of dynamical system theory to analyze particle behavior in this vicinity.

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11. Measurement Technology for Processing of Semiconductors

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Objective: Develop measurement methods, standards, and data to characterize and/or control processing reactors used by the semiconductor industry for (1) electrical and RF parameters relating reactor control variables to plasma conditions, (2) ionized and neutral species concentration measurements, and (3) wafer surface state.

Problem: Design and operation of processing reactors is changing from a completely empirical basis to one strongly dependent upon process and reactor modeling. The semiconductor industry's long term objective, reflected in the SIA's 1994 National Technology Roadmap for Semiconductors, is model-based design and control of manufacturing processes. Validation of the models is critical for their acceptance and use by the industry and demands many improvements and advances in our measurement capabilities. Although presently used reactor models simulate physical parameters well, the necessary addition of the complex chemistries found in commonly used manufacturing processes is only just beginning. This will require new measurements which couple external control variables such as pressure, gas flows, operating voltages, currents, and temperatures to spatially and temporally resolved chemical information for both the gas phase and wafer surface. To support model-based control algorithms, next generation reactors will also require new process sensing techniques, again with an emphasis on chemical information.

Approach: Data taken on systems with characteristics similar to production process reactors have the greatest value for verification of model predictions and extension of existing or development of new measurement methods. Simulation of production process reactors in the laboratory is a powerful approach to providing the research community with relevant process conditions and ranges of operating parameter variation. Reference reactors are a means to satisfy

this need. They provide a common basis for comparison of results obtained by models and a well defined basis for comparison of measurement results for both existing measurement techniques and newly developed ones. In the plasma processing community the Gaseous Electronics Conference Reference Discharge Cell (GEC cell) satisfies this need for low-density, plasma-based processes. For chemical vapor deposition (CVD) processes reference reactors are not yet available, although NIST is currently engaged in developing a prototype which may serve as a reference reactor specification. Application and improvement of existing measurement techniques using radio frequency (RF) discharges in the GEC cell is a major effort. Measurement of species concentration, ionized species constituency and energy, RF voltage and current and their relation to plasma conditions, and development of measurement methods for surface physical and chemical state are areas of effort. Many of these are non-intrusive to the plasma and have potential for future application as process sensors for control applications.

Results and Future Plans: Current, voltage, and RF power characteristics of the electrical discharge are primary plasma reactor control parameters and have been the subject of much theoretical and experimental effort. An important goal is development of equivalent circuit models of the discharge and reactor that relate electrical properties (current, voltage, and impedance) to densities, energies, and fluxes of charged species. Both models and improved measurement methods and algorithms have been developed using the GEC cell. Ion energies obtained from electrical measurements and models have been compared with direct ion-energy measurements. Good agreement between the two methods have been attained.

Measurement of plasma chemical concentrations in two dimensions provides data needed to test recently developed multi-dimensional models. We have demonstrated that 2-D laser-induced fluorescence imaging of species formed by reactive plasmas in the GEC reference cell can provide such data. In this study, we employed an Ar plasma with small amounts of added CF_4, O_2, and Cl_2, conditions commonly used for etching silicon. The plasma excitation was monitored by optical emission and by laser induced fluorescence of an excited Ar metastable state. The chemical state of the gas was monitored via the fluorescence of the CF_2 radical, a reactive intermediate in the decomposition mechanism yielding etchant fluorine species. The technique of planar laser induced fluorescence (PLIF), in which a planar laser excitation beam and a gated, image intensified CCD camera are used to measure the fluorescent species, was used to determine the concentration profiles in the vertical plane of the discharge.

A number of future developments are planned. These include (1) *in situ* wafer surface state measurement based on spectroscopic ellipsometry with application both to plasma etching and CVD reactors, (2) development of a prototype spinning disk CVD reactor to serve as a reference reactor, and (3) design and fabrication of a second generation plasma reactor similar to the high density plasma reactors planned for the 300 mm wafer size.

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12. Cavity Ring Down Spectroscopy for Low Concentration Moisture Measurements and Standards

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Objective: Develop absolute quantitative methods for measurement of water vapor concentration in gases in the range 0.5 ppb_v - 1000 ppm_v using ultra-sensitive, optical absorption methods in the near-IR.

Problem: Measurement standards in the low concentration region are available above the 3 ppm_v level. Industrial requirements are currently in the 1-10 ppb_v range and continue to decrease. This is especially true in the semiconductor industry. Gravimetrically based primary standards are available in higher concentration ranges where enough moisture in gas streams can be collected and weighed accurately. Currently gravimetric standards are extended based on thermodynamic methods embodied by precision humidity generators. This approach, however, relies on extrapolated values for the saturation properties of water vapor/air mixtures. Such thermal methods are therefore indirect and cannot be validated over the full range of measurement required. Furthermore, these techniques are also applicable only to moisture content of air, whereas measurements over a wide range of process gases are needed for industrial applications. First-principles-based techniques, that are (1) both accurate and sensitive, (2) cover the required concentration ranges, and (3) are extensible to gases other than air will be developed to extend the range of primary moisture measurement standards.

Approach: Cavity ring-down spectroscopy, (CRDS), realized with state-of-the-art components, is projected to be sensitive to systems having absorption coefficients as low as 10^{-10} cm^{-1}. A high-Q, Fabry-Perot type resonator forms the centerpiece of CRDS. Laser light is injected into the cavity through one end mirror. While this mirror reflects most of the incident light, a small fraction couples into the cavity filling the cavity with an electromagnetic field. When the injected beam is interrupted, the cavity's optical field begins to lose intensity or "ring down" exponentially, with a time

constant determined by both mirror and absorptive losses to the gas filling the cavity. Electromagnetic field intensity is monitored by observing the light transmitted through the second mirror. At laser frequencies tuned to an absorption resonance, the ring-down time is reduced, and the concentration of the absorbing species can be extracted from the reduction in the decay time. It is anticipated that by using state-of-the-art mirrors and lasers, water vapor concentrations of 0.5 ppb_v should be detectable based upon measurement of decay times with 1% accuracy. Sensitivity is maximized by using ultra-low loss mirrors, e.g., 99.9999% reflectivity in near-IR spectral regions where relatively strong overtone rotational-vibrational transitions in H_2O occur.

Results and Future Plans: Performance of a prototype ring-down cavity has been investigated using pulsed lasers to probe the forbidden rotational-vibrational band of O_2 near 760 nm. Both dye and Ti-sapphire lasers have been used to investigate quantitative measurement capability. Models that deconvolute the effects of laser line width, cavity response characteristics, and absorption feature line width have been developed. These, coupled with experimental results, are the basis for successful demonstration of CRDS's capability for quantitative measurement. Measurements of absorption features are quantitative, demonstrating the capability for absolute measurement of absorption line strengths. Use of these methods with the water vapor absorption band near 1.39 μm will require high reflectivity mirrors (1-50 ppm loss) and a frequency stabilized, single mode diode laser or an optical parametric oscillator.

CRDS measurement of rotational-vibrational transitions in water will be coupled with the primary gravimetric standard, to assign accurate, absolute line strengths. These measurement will be made at the higher concentrations (100 to 10,000 ppm_v) where the current primary standard operates. These calibrated line strengths are the basis for extension of absorption measurements over at least 6 orders of magnitude. The optical absorption approach will function as an absolute measurement standard for low concentrations based on the molecular properties of water.

13. Self-Assembled Monolayers for Biosensing

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Objective: Use self-assembled monolayers (SAMs) as model systems to develop fundamental, quantitative knowledge of molecular recognition structures and reactions. Develop and apply characterization methods sensitive to physical and chemical surface properties of single and multi-layer structures to determine structural features and to demonstrate the occurrence of molecular recognition events.

Problem: Future biosensors will be required to perform multi-analyte measurements rapidly, accurately, and at increasingly lower cost. Surface confined arrays of highly selective sensing elements are promising in this regard. For example, array-based screening techniques are being studied for DNA diagnostics and drug discovery; however, the designs are based on purely empirical methods. Relatively little effort is directed toward understanding how the molecular scale structure of these surfaces affects operation of arrays; it is this gap that our work addresses. Additionally, to achieve an improved level of understanding we must develop characterization methods capable of elucidating both the structural properties of biomolecular layers and their molecular recognition reactions.

Approach: Alkanethiol SAMs impart chemical sensitivity to Au surfaces forming robust, ordered structures with highly tunable surface characteristics. The thiol functionality bonds strongly to the gold surface forming a densely packed monolayer with the opposite end of the thiol molecule forming the SAM surface. Fully functional protein and nucleic acid monolayers can be prepared by several methods. Preferred is a self-assembly process where the biological species of interest is modified by thiol derivatization and spontaneously adsorbed on a gold surface.

Attachment to a preformed alkanethiol SAM can also be used where interactions (e.g., electrostatic, hydrogen bonding, etc.) between the SAM and biological species are exploited. Biotin-avidin coupling is also being investigated where biotin-containing SAMs bind the protein avidin, which in turn can couple biotinylated biological molecules. The first method is used in our studies of surface bound DNA, where single strand (ss) DNA is readily synthesized with an attached thiol. Self-assembled oligonucleotide monolayers are then easily prepared by exposing a bare gold sample to an aqueous solution containing the thiol-derivatized DNA. As typified in our studies of DNA, the features of the thiol self-assembly process for biological monolayers include: (1) reproducible preparation, (2) custom tuning of surface properties using a "mixed monolayer" approach by the controlled addition of other alkanethiol molecules, (3) the ability of the monolayers to serve as model platforms to study solid phase biological processes, (4) the production of planar structures that are readily studied using a broad array of surface analytical techniques, and (5) facile patterning of biological species with micrometer-scale control of dimensions using a photolithographic process developed at NIST. Surface sensitive techniques useful for the characterization of SAM-based biosensing surfaces that need to be investigated include surface enhanced Raman spectroscopy, grazing angle FTIR spectroscopy, STM, XPS, and SIMS.

Results and Future Plans: Surface confined hybridization reactions of DNA are the basis of an emerging microchip technology for sequencing and rapid screening of genetic diseases. These devices use the sequence specific hybridization of a single strand (ss) "target" oligonucleotide with surface immobilized ss-DNA probes. The utility of surface-bound DNA probes for gene sequencing and diagnostics has been demonstrated in functional assays. Little is known, however, about the structure of bound probes and how it affects sensitivity and hybridization efficiency. A more quantitative understanding of the surface hybridization process is needed to design efficient probe arrays at lower cost. To gain a fundamental understanding of DNA probe structure and reactivity, we have investigated the immobilization of thiol-derivatized DNA probes on Au surfaces and their associated hybridization reactions. One of our goals in these studies is to determine the effect of DNA probe surface coverage on hybridization efficiency. Probe coverage may be varied by forming two component monolayers of a thiol-modified probe (HS-DNA) and an inert, hydroxy-terminated thiol as a diluent.

A complementary array of techniques has been used to assess DNA surface density, hybridization activity, molecular orientation, and layer thickness. These include x-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) imaging, ellipsometry, fluorescence and infrared (IR) spectroscopies, and ^{32}P radio-labeling. Under development are fluorescence and Raman spectroscopic techniques for imaging of photopatterned arrays. Using the mixed monolayer approach the coverage of immobilized probe can be varied continuously from 0.1 to 1.0 monolayers. Ellipsometry and XPS results indicate that the maximum coverage obtained of 3×10^{13} probes/cm^2 is approximately 1/3 of that expected for a densely packed monolayer of HS-DNA oriented normal to the surface ($\sim 1 \times 10^{14}$ probes/cm^2). Additionally, SIMS spectra of DNA probes on gold surfaces were found to contain relatively intense parent ion signals for cytosine, guanine, adenine, and thymine that were shown with XPS to vary linearly with probe coverage. The high sensitivity of imaging SIMS may be valuable in assessing the quality of DNA probe arrays.

Radio-labeling techniques, using thiol-derivatized ss-DNA probes having specified base sequence, have been used to study hybridization activity of surface immobilized DNA. Control experiments with non-complementary target DNA show that specific hybridization of only the complementary probe occurs. As expected the hybridization was reversed when the melting temperature of the duplex was exceeded. Initial experiments to assess probe coverage effects on hybridization activity used a ^{32}P-labeled target complementary to the bound probe. Maximum hybridization occurred with a probe coverage of approximately ½ the maximum coverage ($\sim 1.5 \times 10^{13}$ probes/cm^2).

The film formation dynamics and physical characteristics of the self-assembly process have been investigated using a UHV STM having molecular resolution. Results from these studies have shown strong dependence of film morphology on molecular structure of the alkanethiols assembled on single crystal gold surfaces. Both the type of alkanethiol, chain length, and Au crystallographic surface orientation strongly affect film morphology. Vacuum dosing experiments have shown 2-dimensional phenomena such as surface defect motion, island shape anisotropies and alignment preferences for monolayers having a reactive terminal group, i.e., C_6OH. Such morphological studies are anticipated to be useful in guiding construction of more complex structures based on the self assembly process.

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14. Gas Sensing with Micro-Hotplate Sensor Arrays

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Objective: Demonstrate the feasibility and manufacturability of silicon micro-machined, thin-film sensor array technology for multi-analyte, real-time detection and concentration measurement of gas phase species.

Problem: Detection and measurement of individual and multiple gas phase species is currently achieved with relatively expensive, ruggedized analytical instruments. Response times vary from a few seconds to 1 - 2 hours. Inexpensive, real-time or near real-time measurement capability with the required sensitivity can provide a sensing and measurement technology of broad utility, e.g., process control, chemical identification/ verification of materials, auto emission measurement, and environmental monitoring.

Approach: Expertise in the areas of metal oxide sensing materials, their deposition as thin films with surface dispersed metal additives, IC design and fabrication, silicon surface micro-machining, and analysis of signal response patterns is combined in developing this technology.

Micro-hotplate chemical sensor arrays are based on substrates consisting of monolithic, CMOS-fabricated, bridge structures formed with post-CMOS process silicon micro-machining. Micro-hotplates are multi-layer structures, designed and patented by NIST, that consist of a heater, a thermometer/heat distribution plate, and sensing film electrical contacts. Typical single element sizes range from 100 to 250 μm. These are easily fabricated in an array format. Device fabrication takes advantage of commercially available CMOS processing providing a path to a manufacturable sensing technology. Electrical conductance response of semiconducting oxide, thin films, e.g., SnO_2, is the transduction method for detection of

chemical species adsorbed on the film surface. These sensor structures provide sensitivity, selectivity, capability for real-time monitoring, low cost, and mechanical robustness. Surface dispersed, catalytic metal additives alter response sensitivity and selectivity of the metal oxide sensing films of individual array elements.

Micro-hotplates have low power requirements, i.e., 10's of milliwatts, large operating temperature range (>800 °C), and heating time constants of 1 - 2 milliseconds. This capability supports a novel sensing approach, temperature programmed sensing, (TPS). TPS on the sub-second scale and in the array context has excellent potential as a chemical species measurement technique for real-time sensing of individual species in multi-component gas mixtures. TPS response signatures are characteristic of adsorbed species/sensing material combinations. Algorithm development is an important aspect of the research effort.

Results and Future Plans: Response data for single chemical species in air have been obtained for a number of species. These include CO, CO_2, ethanol, methanol, propanol, acetone, perchloroethylene, and other organic materials. Extensive data sets are available for CO in air, ethanol, and methanol. These demonstrate both detection limits and response linearity. For CO in air, detection limits have been demonstrated at the 2 - 3 part per million level with good linearity up to 1000 ppm. Long term testing of individual micro-hotplates for approximately one year demonstrate sensitivity and the reproducibility of TPS response patterns over long time periods.

TPS response pattern recognition algorithms are the means to identify and measure concentration of single and multiple species. Methods are under development to differentiate between species having similar and dissimilar response patterns. To date response data on single species in air show promise. Continued efforts are expected to produce algorithmic methods that differentiate between similar species, e.g., between ethanol and methanol, in additional to recognizing species with strongly dissimilar patterns.

Deposition of different oxides on individual elements of a 4-element array has been pursued using a chemical vapor deposition (CVD) process. Thermal CVD of SnO_2 on individual array elements has been demonstrated. Sensing films deposited in this manner show good sensitivity and response characteristics. Procedures for deposition of catalytic metals, e.g., Pd, Pt, and Ni, and additional metal oxides, ZnO and TiO_2, will be developed.

Continued work in FY96 is planned in the areas of robust and reliable sensing film electrical contacts, optimization of TPS programming to maximize detection sensitivity, 4-element array response testing in 2 and 3 component mixtures, deposition of catalytic metals and oxide materials, and replacement of aluminum with tungsten in the micro-hotplate structure to improve sensing electrical characteristics and to attain higher TPS temperatures.

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15. *Engineering Measurements for Hydrothermal Processes*

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Objective: Near-term objectives are the development of *in situ* measurement techniques that identify reaction and corrosion intermediates, and allow the mapping of velocity and thermal profiles, while withstanding the aggressive hydrothermal environment. In the longer term, data gathered will be used for developing on-line process controls and engineering design models.

Problem: Hydrothermal processes range from treatment of industrial wastes to power generation in boilers. Major challenges to the large scale implementation of these processes include inadequate destruction of refractory (thermally resistant) compounds, vessel corrosion, salt deposition and scaling, a poor understanding of the near-critical heat and mass transfer, and a lack of on-line process sensors and engineering models. To overcome these challenges, it is necessary to understand and develop engineering models for the chemical reactions, transport phenomena, and thermodynamics in this medium. However, investigations have been limited by a lack of robust, *in situ* measurement techniques that can withstand the oxidizing, high temperature, high pressure, and high gradient environment. Thus, the problem is to understand and model these important hydrothermal processes through development and application of *in situ* measurement techniques.

Approach: Each project in the program addresses a major challenge (*i. e.,* corrosion, refractory waste, salt deposition, transport phenomena). For understanding corrosion processes and validation of other reaction mechanisms, Raman spectroscopy will be used to identify key species. For developing refractory waste destruction models, oxidant substitution and mixing strategies will be investigated, with results being quantified via an *ex situ* (effluent) analysis for total carbon and by gas chromatography. For studying salt deposition and heat transfer processes, which are relatively new projects, experiments under various flow regimes and chemical compositions will be devised, and will employ several visualization and measurement (*e.g.,* videography, schlieren, LDV, thermocouples) techniques. The salt deposition experiments will also provide phase boundary data, which will support thermodynamic modeling efforts.

Results and Future Plans: During FY95, we performed the first *in situ* observation of corrosion spinels in supercritical water via Raman spectroscopy. The discovery that *in situ* species are different than those observed *ex situ* offers the potential to enhance our understanding of corrosion processes. These results underlie our ongoing industrial collaborations with Babcock & Wilcox and the Electric Power Research Institute. In this collaborative project, we developed techniques to quantify species in multicomponent mixtures as a function of temperature, and assisted in the design of an optical probe for *in situ* chemical detection in crevices.

Waste destruction experiments to support model development have also been conducted through multiple collaborations. For the Naval Surface Warfare Center, two new strategies for ammonia (a refractory waste) destruction have been devised: oxidant substitution and mixing with another refractory (acetic acid). In 650 °C solutions with hydrogen peroxide, over 90% destruction was achieved versus the 50% levels achieved with oxygen, which conflicts with the assumption that peroxide simply serves as a source of oxygen. Mixing strategies are also important. In 500 °C mixtures of ammonia and acetic acid, ammonia destruction rose to nearly 80%, versus the 38% conversion in solutions without acid. In both cases, the acid was destroyed to over 90%. In a different collaboration with Conoco on industrial wastes, *in situ* spectroscopic investigations revealed that breakdown of methylene chloride, a common industrial solvent, surprisingly occurred below 200 °C even in the absence of oxidizer. Spectroscopic investigations in another collaboration with the University of Hawaii demonstrated that for simple alcohols, which are

intermediates in the biomass conversion process, dehydration reactions persisted up to 500 °C, which is much higher than the 330 °C limit postulated based on *ex situ* effluent analyses. These results illustrate the benefits of developing and using *in situ* techniques and their potential impact on the operation of hydrothermal processing systems.

Research efforts will continue in FY96, in the areas of measurements for corrosion control, salt deposition and heat transfer. An instrumented optical cell for the *in situ* analysis of oxide phase behavior, as a function of pH and electrochemical potential, is being developed for an emerging corrosion control program with the Massachusetts Institute of Technology (MIT) and the Pennsylvania State University. For the salt deposition work, a new, low-cost flow cell which will be used to generate data on mass transfer and flow profiles for computational simulations, as well as thermodynamic phase-boundary data has been designed and constructed in collaboration with MIT. These thermodynamic data will also support a new three-phase, modified thermodynamic model for the sodium sulfate/water system. Plans are also underway to elucidate heat transfer processes near the critical point with a new hydrothermal heat transfer facility, which will incorporate visualization techniques being developed collaboratively at the University of California - Irvine.

Publications:

Allmon, W.E, Hurst, W.S., Bowers, Jr., W.J., Bean, V.E., and Millett, P.J., "**Spontaneous Raman Spectroscopy for Power Plants,**" Physical Chemistry of Aqueous Systems: Meeting the Needs of Industry, Proceedings of the 12th International Conference on the Properties of Water and Steam, Ed. by H. J. White, Jr., et al., Begell House, New York, (1995).

Bowers, Jr., W.J., Bean, V.E., and Hurst, W.S., "**Optical Windows for a Flow Cell to Contain Aqueous Solutions at High Pressure and Temperature,**" Rev. Sci. Instrum. 66, 1128 (1995).

Ochel, H., Bean, V.E., Bowers, Jr., W.J., Davis, R.W., and Hurst, W.S., "**Optical Probing of Hydrothermal Reactions and Flow Patterns in a High-Pressure Flow Reactor,**" Physical Chemistry of Aqueous Systems: Meeting the Needs of Industry, Proceedings of the 12th International Conference on the Properties of Water and Steam, Ed. by H. J. White, Jr., et al., Begell House, New York, 660 (1995).

16. *Spray Combustion and Emissions*

***C. Presser**, A.K. Gupta (Univ. Maryland), C.T. Avedisian (Cornell), A. Nazarian (SAIC), S.R. Charagundla, C. Cook, R. Aftel (Univ. Maryland), B. Shomaker, H. Steffen (Univ. Maryland), C. Connon (Univ. California -Irvine), V. Venkataramanan (Ohio State Univ.), A. Chen (Univ. Notre Dame), and T. Devlin (Jackson&Tull)*

Objective: Develop the technology to measure and explore the feasibility of correlating the interrelationship between operating conditions, spray flame characteristics, and formation of toxic emissions in reacting thermal systems.

Problem: Control of combustion efficiency and exhaust emissions from industrial thermal reactors that are used for power generation and treatment of process liquid chemical wastes, is generally based on *a priori* knowledge of the input stream global physical and chemical properties, desired stoichiometric conditions, and monitoring of a few major chemical species in the exhaust. In general, there is a dearth of data on conditions within the reactor, and in particular, on the quality of the atomized liquid spray. It is precisely this region that requires a better knowledge base to enable optimization of the chemical and thermal processes, and minimization of particulate and toxic emissions. System performance is dependent strongly on liquid atomization, aerodynamic design, and the degree of liquid/air mixedness. The need to provide *in situ*, real-time data on the characteristics of the droplet field, and its interrelationship with the system operating conditions (e.g., desired stoichiometry) and particulate/toxic emissions is crucial to the efficient operation of thermal reactor systems.

Approach: The approach is threefold: 1) expand the capabilities of the NIST spray combustion facility (SCF) to handle different process liquid fuels and wastes, atomizer designs, and combustor configurations; 2) develop/apply a variety of diagnostics to the input fuel stream (fuel composition), spray flame (droplet size, velocity, and temperature), and combustor exhaust (particulate and toxic gases); and 3) provide data for input/validation of numerical simulations.

Results and Future Plans: In FY95, the program was redirected to address issues relevant to the atomization and combustion of liquid wastes in the NIST SCF. During this transition phase, upgrade of the facility included improvement of the diagnostic capabilities and examination of state-of-the-art liquid fuel injection concepts. To measure toxic emissions, a confinement chamber and HCl scrubber were designed for the spray burner. An on-line FTIR spectrometer was installed for extractive sampling of chemical species, and optics were procured for measurement of soot concentration via laser induced incandescence (LII).

Since fuel atomization is an essential component of this program, we focused our efforts to study a variety of atomizer designs, namely: 1) acoustic atomization (with Fluid Jet Associates), 2) electrostatic atomization (with CFD Research Corp.), and 3) gas/steam-assisted atomization (with the University of Maryland). In our collaboration with Fluid Jets Associates, a commercially available pressure-jet nozzle that was modified with an acoustic driver, was used to sustain a kerosene flame in our spray combustion facility. The acoustic driver did not provide any visual changes to the global structure of the flame, except for an observed change in the spray angle immediately downstream of the nozzle exit. The most significant advantage of the acoustic driver is expected to be with regard to emission levels. We are currently evaluating gas sampling measurements of NO_x, CO, and CO_2 to confirm our expectations. In addition, analysis of droplet transport in a kerosene pressure-atomized spray flame was carried out using phase Doppler interferometry to determine local droplet velocity and direction. This information has provided an in-depth understanding of the effect of the swirling gaseous flow field on the drag and dispersion of individual droplets of various sizes.

We also collaborated this year with the Naval Surface Warfare Center to investigate the destruction of shipboard wastes via vortex incineration technology. We demonstrated the

capability to provide future measurements in flames laden with wastewater in the SCF. In this preliminary stage of the program, phase Doppler size/velocity measurements were carried out, as well as measurements of NO_x, CO and CO_2 in kerosene flames with and without water (acting as a surrogate for wastewater).

Development of a laser-driven thermal reactor was initiated with SAIC to provide thermodynamic and kinetic information on waste fuels. This technology will be used for on-line monitoring of fuel thermal content and composition before introduction to the burner. We also initiated a collaboration with Jackson & Tull to develop a process data acquisition and control system for the spray combustor.

In FY96, we expect to complete confinement of the spray burner, fabrication of the gas emission measurement train, and assembly of the LII system. We will also continue our evaluation of different liquid fuel/waste atomization technologies, and the interrelationship of the spray characteristics with operating conditions and particulate/toxic emission levels.

Publications:

Presser, C., Gupta, A.K., Hodges, J.T., and Avedisian, C.T., "**Dispersion of Droplets in Swirling Spray Flames**," in Fluid Mechanics and Heat Transfer in Sprays, FED-233, HTD-321, Am. Soc. Mech. Eng., New York, NY, 565-575 (1995).

Gupta, A.K., Presser, C., Hodges, J.T., and Avedisian, C.T., "**The Role of Combustion on the Transport of Droplets in Pressure-Atomized Spray Flames**," Journal of Propulsion and Power (in press).

Presser, C., Gupta, A.K., Hodges, J.T., and Avedisian, C.T., "**Behavior of Droplets in Pressure-Atomized Fuel Sprays with Coflowing Air Swirl**," AIAA Progress Series on Recent Developments in Spray Combustion (in press).

IV. Surface and Microanalysis Science Division (837)

Rance A. Velapoldi, Chief

A. Division Overview

Mission:
The **Surface and Microanalysis Science** Division conducts research and development to: (a) determine the **chemistry and physics of surfaces, interfaces, particles, and bulk materials**, and their interactions with a broad spectrum of species including electrons, photons, ions, atoms, and molecules; (b) determine the **chemical and isotopic composition, morphology, crystallography**, and **electronic structure of materials** at scales ranging from mm to nm; (c) determine the energetics, kinetics, mechanisms, and effects of processes occurring on solid surfaces as well as within materials (or devices); (d) study the total **chemical measurement process** as well as **pollutant source apportionment** in **atmospheric chemistry** using **chemometrics**; and (e) develop and certify Standard Reference Materials and Standard Reference Data. Emphasis is placed on performing fundamental and applied measurement research, providing data and standards (including software), and developing theories that are needed for accurately measuring chemical composition and dynamic processes that occur on surfaces and in microstructures. This information establishes the relationships between chemical composition and processing, devices, or material properties and provides the basis for advances in various technologies, such as chemical catalysis, advanced electronics, and materials science.

Programs:
In this overview, some general comments will be presented on our major initiative and trends and our accomplishments in the four areas of **chemical and morphological measurements** at **high spatial resolutions, surface dynamical processes, atmospheric science**, and fundamental measurements.

General Comments. The Surface and Microanalysis Science Division is well-positioned to contribute to the advanced measurement needs represented in CSTL's strategic thrusts of Fundamental Measurement Science, Process Technology, Environmental Technologies, Biotechnology, and Health Care Technology. The importance of chemical and morphological characterization of a broad spectrum of materials and electronic devices at the nanometer scale and at ultra-low species concentrations continues to be underscored in various reports including the update of the SEMATECH Technology Roadmap and at several NIST Workshops on "Nanotechnology", "Magnetics: Measurement Challenges and Opportunities at Small Length Scales", and the most recent held during November 1995, "Micro Electro Mechanical Systems". Our unique capabilities in microprobe and surface measurement science allow us to make state-of-the-art quantitative measurements at high spatial and temporal resolutions, providing a measurement infrastructure required to support existing and emerging industrial technologies. Our objective is to help develop the next generation tools that push the measurement envelope (*enabling technology*) and, through collaborative research, to apply these new tools internally to NIST programs and externally to industrial and other government agency needs. To this end, we continue increasing, on a limited scale, the measurement capabilities that comprised our major budget initiative proposed in early 1995 to develop a "**National Facility for Chemical and Materials Microanalysis**". These efforts focus mainly on chemical and morphological sample characterization, generally at high spatial resolution, and investigations of surface interactions.

Spatially Resolved Chemical and Morphological Analyses. One of our main objectives over the past several years has been to provide measurements methods, standards, and data required for **accurate microprobe analyses**. As bases for these measurements, we pushed the measurement envelope for electron, ion, and photon probe techniques in terms of spatial resolution and

chemical concentration, developing various data calculation capabilities (from FrameC to DeskTop Spectrum Analyzer) and making measurement breakthroughs over the years (ranging from elemental and molecular compositional mapping to trace nanoanalysis). This year we have determined the measurement parameters to increase accuracy and applied these techniques to materials used in a broad spectrum of technologies. For example, in applications we have: measured separate iron and silicon signals from chemical species within 10 nm of each other in small spheres (20-40 nm in diameter) to understand how magnetic materials form during flame generation; calculated **phase compositional maps** from elemental electron probe data for high temperature superconductors, important in understanding the quality and presence of superconducting phases in thin films; measured implant distributions and diffusion of many elements in materials (GaAs, Si, Si/Ge, SiC, GaN) critical to the semiconductor and electronics industries; characterized yttrium-doped ZrO_2 powders using micro-Raman and electron probe methods; measured SrS and similar compounds in films with potential as optical storage devices; established **molecular compositional maps** for DNA probes on thin-film surfaces, organic compounds on hair, and cosmetic agents on skin; and measured ^{44}Ca concentrations in apple skins to understand increases in apple shelf life when washed with calcium-containing chemicals. This information would not be available unless earlier work had not extended measurement capabilities.

We are continuing to develop advanced technologies that address measurement community needs. In instrumentation, we are working with X-Ray Optical Systems to develop and rigorously test optics to **focus x-rays** with the objective of providing a transferrable measurement system that covers the 1-100 μm range for materials. In a similar vein, we are working with M.E. Taylor Engineering to develop a **low magnification detector** for use in the environmental scanning electron probe, which will provide a larger visualized area. Efforts continue also on correlating the data obtained from the NIST-developed **scanning scattering microscope** with **atomic force microscope** data to define measurement parameters. This system will then be applied to elucidating the morphology and structures on the surfaces and interfaces of silicon-based semiconductors.

To address the increasing need to obtain chemical information resolved in three dimensions, we are performing research to move from the current pixel-based, two dimensional representation of chemical concentration to a **voxel-based, three dimensional** representation. This capability requires measurement techniques that not only raster horizontally over the sample to produce elemental and molecular compositional maps in the x and y dimensions, but also measure the chemical concentration as a function of depth in the third 'z' dimension. Efforts have successfully focused on obtaining this third dimension with secondary ion mass spectrometry. Simultaneously, we are developing the calculation and data manipulation tools to present and visualize data in multidimensions. For example, multidimensional representations are used for the presentation of concentration data in histogram space in which the axes represent composition while the data are tied to dimensional x,y,z (volume) space. Additional dimensional variables such as time can also be included in advanced displays of this **multifaceted information space**.

Increasingly we have found it useful to **automate microprobe analyses** for particle samples, providing "particle population fingerprints", useful in identifying particle types (similar chemical species), sources, uses, and manufacturing processes. To this end we have established necessary measurement parameters and their effects on determining individual particle populations in samples. We are currently developing visual data presentation methods that will provide procedures to visualize and identify these "fingerprint" populations.

To answer a need for obtaining accurate data on critical particle and other targeted samples with rapid turnaround, we developed an integrated, multi-probe analysis procedure that reduces our measurement response time by an order of magnitude from approximately ten days to one day.

In FY95, we were successful in obtaining NIST Competence funding to develop a **near-field**

scanning optical spectroscopy capability for our proposal "*In situ* Nanoscale Probes of Catalysts and Catalytic Chemistry". This work will begin in FY96 and will combine our expertise developed in non-linear optical spectroscopy to provide a laser probe with intense, broad-band infrared radiation. The objective of this long term effort is to give chemical/molecular information on the tens of nanometer spatial scale with a measurement tool that is non-destructive. If successful, this effort will push the measurement envelope to higher spatial resolutions, an integral component of our National Facility Initiative.

Dynamic Surface Processes. Our efforts in dynamic surface processes during the past several years have led to state-of-the-art measurements in **femtosecond infrared spectroscopy**. Through these measurements and a comprehensive theory development, we have shown that photon stimulated surface reactions can be explained by a single, **hot-electron transfer** process which subsequently activates two distinct **reaction mechanisms** in surface adlayers. This information will be critical to predicting surface reactions and tailoring surfaces for specialized functions. Extending these successes with single photon absorption, we are carrying out measurements and interpreting results to explain current theories of ultrafast multiphoton absorption and energy transfer.

We have also applied our measurement expertise to form and deposit superconducting films on surfaces in reactive atmospheres; investigate H_2 plasma processing of GaAs surfaces for oxide thin-film growth in the semiconductor area; characterize oxides of GaAs using non-linear optical techniques; determine ordering of liquid crystal alignment layers using second harmonic generation; and provide insight into the oxidation of silicon surfaces with water using infrared probes.

We plan to apply our unique probe measurement capabilities to characterize metal ions on **single site catalytic materials** such as crystalline zeolites and investigate reaction processes on these types of surfaces. This is a natural progression from our infrastructure research on gas adsorbate-metal crystal substrate energy transfer mechanisms and surface reactions, while our new competence project will be a major step in providing measurement tools and infrastructure research required by measurements for the **catalyst** and **catalytic chemistry** areas.

Atmospheric Science. In the atmospheric chemistry area, we continue to extend our efforts in atmospheric measurements, standards, and **pollutant identification and source apportionment**. During the last several years, we established the capability to make carbon isotopic measurements on carbonaceous samples (gases and particles) that were three orders of magnitude smaller than were previously required. This advance was coupled with in-depth elucidation and optimization of carbon production from various species in preparing samples for accelerator mass spectrometry measurements, detailed sampling strategies, and investigations on the effect of multivariate blanks. These unique measurement capabilities and close collaborations with local, state, and national governments, have led to the analysis of pollutants and their sources to aid in the selection of **control strategies for pollutant reduction**. In FY95, for example, collaborative measurements on local (Denver, Albuquerque) and regional (Los Angeles Basin) scales were successful in providing potential pollution control strategies for Denver and identified fast food cooking as a significant pollution source in the L.A. Basin. These studies are being expanded from local and regional scales to a global scale with our current collaborative efforts with the University of New Hampshire, NASA, NOAA, and NSF to measure aerosols (particles and gases) trapped in ice core samples from Greenland to obtain an historical record of atmospheric pollutant conditions and deposition. Additional work in source apportionment including combustion and vegetative emission relied on determining the organic species and carbonaceous gases formed during combustion or present in samples, identifying **ozone precursors**, measuring possible isotopic fractionation (^{13}C, ^{12}C), determining particle morphology and chemical phases, providing isotopic data bases, and developing reference **carbon isotopic standards** (gases and particles) to be used in the quality assurance of these measurements.

Our long-term collaborative research efforts with EPA and several foreign government laboratories to provide a network of **Primary Standard Reference Ozone Photometers** used for national and international ozone monitoring has resulted in the production of several new instruments as well as updating and calibrating existing photometers against the NIST primary instrument. New photometers were built for Canada, the Czech Republic, and a second for Switzerland. We are developing a photometer for the Physicalische Technische Bundesanstalt (PTB) in Germany, and continue to get inquiries from other government laboratories in various countries (England, France, and Australia). This small program continues to demonstrate exceptional leverage in establishing traceability of international ozone measurements to NIST. The NIST-built photometer at the Swiss Federal Laboratories for Materials Testing and Research has been designated as the **primary standard** by the World Meteorological Organization for their extensive surface ozone measurement program in Europe and Africa.

Fundamental Measurement Science. Although fundamental measurements, standards, and data are intrinsic to each of the first three areas, they also are important to consider separately in our efforts to establish traceability on national and international scales. Research considering univariate and multivariate parameters on each step in the total measurement process increases our understanding of the process and thus helps establish an accurate measurement infrastructure. Significant events in FY95 that provide (and transfer) this measurement infrastructure included: held a workshop and performed **Monte Carlo calculations** to increase accuracy in electron probe analysis; performed research and published basic papers on trace nanoanalysis and pitfalls in **standardless electron probe analysis**; performed 'first principle' calculations of standard x-ray intensities in the NIST-NIH DTSA and issued **DTSA Version 2**; defined multivariate blank contributions to atmospheric measurements; increased accuracy of isotopic ratio measurements on atmospheric gases by a factor of ~2; studied individual pulse analysis in low level nuclide counting to understand process and increase sensitivity; and established **analytical model** for **adsorbate photodesorption**. We have interacted extensively with the national and international measurement communities to provide aid in agreement of terminologies (harmonization of ISO and IUPAC **analytical terminology**, concepts, and formulation for **detection and quantitation limits**) and establish traceability (standards, data, round robins, measurement procedures and draft standards). These latter efforts have ranged from work on a particles-in-oil standard (with the National Fluid Power Association), to an international Secondary Ion Mass Spectrometry (SIMS) round robin using the NIST SRM to compare measurement accuracies among laboratories, to comparing and defining methods for reporting uncertainties in airborne asbestos measurements using transmission electron microscopy, and finally to developing improved reference data and procedures for AES and XPS. These efforts have been performed with a variety of organizations including ASTM, ISO, IUPAC, and VAMAS.

Many of the specifics for these technical contributions can be found in the following section.

B. Selected Technical Reports

1. *Improved Reference Data and Procedures for Surface Analysis by Auger-Electron and X-Ray Photoelectron Spectroscopies*

C.J. Powell

Objective: To provide reference data and reference procedures that are needed to improve the accuracy and efficiency of surface analyses made by Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS).

Problem: AES and XPS are two of the most commonly used techniques for surface analysis but the measurement accuracy is presently poor in comparison to many other analytical techniques. Interlaboratory comparisons have demonstrated inadequacies in the calibrations of the binding-energy (BE) scales in XPS and the kinetic-energy (KE) scales in AES; such calibrations are particularly needed for the reliable determination of chemical state from the so-called chemical shifts of elemental peaks. Improved reference data, particularly for chemical shifts in XPS, inelastic mean free paths (IMFPs), and elastic-electron-scattering cross sections, are needed for qualitative analyses by XPS, correction for matrix effects in quantitative analyses in AES and XPS, and correction for the effects of elastic electron scattering in AES and XPS, respectively. Finally, reference procedures are needed to guide analysts in making AES and XPS measurements with the desired accuracy and efficiency.

Approach: An improved procedure has been developed for the calibration of the BE scales of XPS instruments and tested with an interlaboratory comparison. An agreement has been established with the Russian State Metrological and Certification Analytical Center (ANTECH) for the provision of evaluated BE data from published papers for the NIST XPS Database. NIST has purchased an elastic-electron-scattering cross-section database from two experts, A. Jablonski (Institute of Physical Chemistry, Poland) and S. Tougaard (Odense University, Denmark). New calculations of IMFPs are being made with an improved algorithm developed by D. Penn (PL). A new method for simulating the transport of signal electrons in XPS has been applied to determine the dependence of the mean escape depth (MED) on the elemental line and the experimental configuration.

Results and Future Plans: The improved procedure for calibrating the BE scales of XPS instruments was discussed at recent meetings of ASTM Committee E-42 on Surface Analysis and ISO Technical Committee 201 on Surface Chemical analysis, and will be integrated with an independent proposal from the UK National Physical Laboratory. It is planned to extend this work to calibration of the KE scales of AES instruments. Version 2 of the NIST XPS Database with improved software and increased data is scheduled for release in 1996. The new elastic-electron-scattering cross-section database will be released in spring, 1996. New calculations have been made of IMFPs for the rare earth elements, dysprosium and gadolinium, to resolve uncertainty in applying the NIST-developed predictive IMFP formula for rare earths and an apparent conflict arising from recent measurements of absolute Auger yields for these elements. It is planned to prepare a database of IMFP values for elements and compounds that have been determined using the Penn algorithm, and means for estimating IMFPs for other materials. MED values have been found to be typically about 30% less than those expected if elastic-electron scattering effects were ignored, although much larger differences (increases of up to a factor of two) could occur for uncommon measurement configurations.

Publications

Powell, C.J., "**Energy Calibration of X-Ray Photoelectron Spectrometers: Results of an Interlaboratory Comparison to Evaluate a Proposed Calibration Procedure,**" Surf. Interface Anal. 23, 121 (1995).

Powell, C.J., "**Elemental Binding Energies for X-Ray Photoelectron Spectroscopy,**" Appl. Surf. Science 89, 141 (1995).

2. *Quantitative Electron Probe Microanalysis: Using "First Principles" Calculations of Standard X-ray Intensities in NIST-NIH Desktop Spectrum Analyzer*

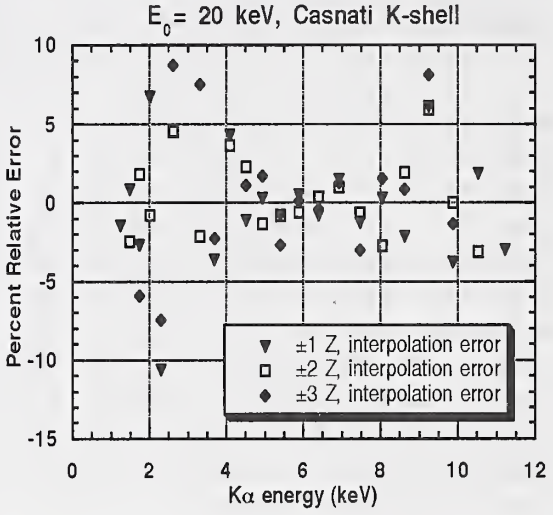
D. Newbury, R. Myklebust, and C. Swyt (National Institutes of Health)

Objective: Develop and test techniques to incorporate theoretically calculated standard intensities into a quantitative x-ray microanalysis procedure.

Problem: The central paradigm in quantitative electron probe x-ray microanalysis is the measurement of the ratio of the intensity of an element in the unknown to the intensity for the same element in a standard under constant conditions of beam energy, known dose, and spectrometer performance. Usually a pure element or binary compound can be found to serve as a standard, but there are occasions when a suitable standard is not available in the laboratory for direct measurement, or it is not practical to do so. Examples of the latter case include inert gases and radioactive elements.

Approach: Desktop Spectrum Analyzer (DTSA), the NIST-NIH comprehensive software engine for electron-excited energy dispersive x-ray spectrometry, incorporates a unique and powerful spectrum simulation algorithm. Through first principles calculations of x-ray production, propagation, and detection, the analyst can simulate the spectrum that would be measured from any specified composition, at known dose, and for user-selectable detector characteristics. While this is a useful capability, the accuracy of the simulation is strongly affected by the choice of the inner shell ionization cross section, especially for L- and M-shell x-rays, as well as the modeling of the detector efficiency. Moreover, critical parameters such as the fluorescence yield, the ionization fraction that results in photon emission, are not well known for these shells. In the past year, we tested the accuracy of DTSA spectral simulation by making extensive comparisons with experimentally measured spectra from both single element and multi-element standards.

Results and Future Plans: A method was developed to improve the accuracy of simulation for practical analysis situations. When a particular standard is unavailable but pure element standards of similar atomic number above and below the missing standard can be measured, an interpolation procedure based on the measured and simulated standards is used to calculate a correction factor which can be applied to the calculated missing standard. The relative errors that arise from interpolation between two standards located at $\pm\Delta Z = 1, 2$, and 3 atomic number units are shown in the figure for K-shell x-rays. Relative errors in intensity are generally less than ±10 percent. Larger errors are observed for L- and M-shell calculations. Future work is planned to improve the accuracy for these shells.



Publications:

Newbury, D., Myklebust, R., and Swyt, C., **"The Use of Simulated Standards in Quantitative Electron Probe Microanalysis with Energy-Dispersive X-ray Spectrometry,"** Microbeam Analysis 4 (1995) 221-238.

3. *NIST Contributes to ISO/IUPAC Joint Position on Terminology, Concepts, and Formulation for Detection and Quantification Limits*

L.A. Currie

Objective: Paralleling the urgency to develop a uniform international position on Measurement Uncertainty, there has been a long-standing need for a sound, uniform basis for addressing the concepts underlying Detection and Quantification, and for a common system of nomenclature in metrology. International consensus is now at hand as a result of harmonization efforts of the International Union of Pure and Applied Chemistry (IUPAC) and the International Organization for Standardization (ISO).

Problem: The importance of establishing international guidelines on detection and quantification capabilities of measurement processes has been recognized for decades among chemists, but the issue has become more critical in recent years in light of international trade and chemical safety. Perspective on the situation prior to IUPAC/ISO harmonization efforts is given by the statement of the chairman of ISO TC69, "There is an urgent need for answers ... a growing number of regulations and recommendations of the European Community concerning limits ... for trace constituents in food, water, air and soil ... almost all lack a reliable background [on] 'detection limits.'". Within the chemical community one would find the basic capability of a specific chemical measurement process to detect a given toxic contaminant in food or water to appear to vary over a wide range simply because of differing, and frequently unstated "recipes" used for calculating a "detection limit." In addition, the same term would be given quite different meanings by different groups.

Approach: During the last several years, IUPAC and ISO separately initiated efforts to resolve the issues of detection and quantification capabilities in chemistry and in metrology in general. As of late 1992 communication between the two international organizations revealed that, although similar concepts were being developed, totally different terminology was evolving. Harmonization efforts were initiated with a "landmark" meeting between members of ISO and IUPAC in Washington, DC in July 1993. In the following two years, both organizations developed documents reflecting the harmonized concepts and nomenclature, and a second follow-up meeting to resolve remaining issues took place between the IUPAC and ISO representatives. The international recommendations for chemical metrology were published, and those for metrology in general are in an ISO document with a voting deadline of 4 November 1995. IUPAC Recommendations and ISO Standards have enormous impact internationally, and documents undergo intense scrutiny by experts before they are published. As a result, the importance of harmonization between the two organizations cannot be overstated.

Results and Future Plans: The consensus achieved between ISO and IUPAC is reflected in the respective documents of the two organizations. NIST was represented in this effort by L.A. Currie (837) and M.C. Croarkin (882) who attended both harmonization meetings. The IUPAC recommendations concerning detection and quantification concepts and nomenclature are now published. For chemical metrology the future course is already evolving, partly as a result of a presentation of the IUPAC Recommendations at an international forum of chemists, statisticians and regulators at the International Conference on Environmetrics and Chemometrics in September 1995. Plans, as a consequence of that forum and the publication of the IUPAC recommendations, are: (1) publication of the results of the harmonization efforts in *Chemometrics and Intelligent Laboratory Systems*; (2) distribution of copies of the IUPAC document to some 100 people involved in the ASTM D19.02 Task Group on Detection and Quantitation, which meets in Florida in Jan. 1996; and (3) presentation of the concepts at an all-invited session of the American Statistical Association Section on Statistics and the Environment in Chicago in August 1996. These efforts in the U.S. toward dissemination of the new international consensus are bound to be paralleled abroad and true harmonization worldwide should result.

Publications:

Currie, L.A., "Nomenclature in Evaluation of Analytical Methods including Detection and Quantification Capabilities (IUPAC Recommendations 1995)," Pure and Applied Chemistry 67 (1995) 1699-1723.

4. *Isotope Effects Discovered in the Formation of Carbonaceous Aerosol*

L.A. Currie, G.A. Klouda, and B.A. Benner (839)

Objective: To investigate experimentally the nature and magnitude of isotopic and organic fractionation effects occurring in the combustion of representative fuels to form aerosols. Such information is critical for determining fossil and biomass burning impacts on regional pollution and global climate.

Problem: Little, if any, knowledge exists on combustion induced isotope effects, especially as related to organic products of incomplete combustion. Since incomplete combustion provides the opportunity for kinetic isotope effects to manifest themselves, and because of the increasing use of isotopic and organic measurements to characterize major episodes of biomass burning, we designed a laboratory experiment to attempt to detect isotopic fractionation, if present, and to investigate the possibility of linked isotopic-organic fractionation processes. Apart from its basic importance, the information could provide a powerful new measurement tool for the characterization and tracing of natural and anthropogenic combustion aerosols and gases in the atmosphere. (Work supported in part by NASA and performed in collaboration with BFRL and the U.S.G.S.)

Approach: The experiment was designed to examine isotopic and organic fractionation that might occur in a representative set of fuels which are found in natural and anthropogenic combustion processes, such as C_3 and C_4 (photosynthetic cycle) woods and grasses, as well as liquid and gaseous hydrocarbons. Replicate samples of source materials used in the first phase of the study included oak, pine, C_4 plants (tripsicum grass, cane leaves), paraffin, and butane. Products collected included CO_2, CO, and carbonaceous aerosol. Isotopic fractionation was monitored by measuring the abundance of the stable isotope ^{13}C in the fuels and selected combustion products. Ancillary data concerning the stage of combustion, weight loss, and heat evolution were obtained with the NIST

Cone Calorimeter facility. The extreme sensitivity and precision requirements of the experiment were met by using: (1) the NIST Environmental Specimen Bank facilities to produce isotopically homogenous wood and grass specimens, (2) Supercritical Fluid Extraction Chromatography for on-line extraction - GCMS analysis of polycyclic aromatic hydrocarbon (PAH) products, and (3) state-of-the-art isotope ratio mass spectrometry for unusually high precision ^{13}C abundance measurements. The resultant isotopic-organic (PAH) multivariate data were examined for independent and correlated effects, as well as dependencies on fuel type and combustion stage.

Results and Future Plans: Key findings of the research were the discovery of significant ^{13}C isotopic fractionation associated with the transformation from carbonaceous fuel to "soot," and an apparent relationship between ^{13}C isotopic fractionation and PAH molecular patterns. If the relationship is verified in future experiments, it will be a powerful chemometric tool for isotopically "stabilizing" PAH patterns for source recognition.

Crucial to the studies were the abilities to: (1) quantify CO, CO_2, aerosol carbon, PAH, and ^{13}C abundance as a function of fuel and burn stage (smolder, flame, glow); (2) measure ^{13}C abundances to a precision (standard uncertainty) of *ca* 0.01 per mil, since fractionation effects found were as small as *ca* 0.1 per mil; (3) measure PAH combustion products at levels of 100 pg or less; and (4) prepare isotopically homogeneous biomass fuel samples. [Note: the cryo-homogenized woods and plant materials represent the first known prototypes of isotopically homogeneous vegetative reference materials].

Future work will be directed toward the extraction of fuel and burn stage data on inorganic species, plus elemental and extractable organic carbon; and on shedding more light on an interesting aspect of the ^{13}C fractionation, namely a reversal of sign for the hydrocarbon fuel isotopic fractionation, as compared to that of the plant materials. Ultimately, this research will affect the scientific and cost effectiveness of atmospheric sampling-measurement strategies, and further improve our ability to distinguish the chemical impacts of natural and anthropogenic sources on regional and global atmospheres.

Publications:

Currie, L.A., Klouda, G.A., and Benner, B.A. "Multivariate Tracers for Aerosol Carbon: Relation to Source Material, Formation Conditions, and Chemical Robustness, "**Symposium on Clouds, Aerosols, and Radiation,**" Amer. Geophys. Union (Baltimore, June 1995).

5. *Fully Automated Ozone Calibration with the NIST Standard Reference Photometer*

J.E. Norris and E.M. Eijgenhuijsen (Twente Univ., Netherlands)

Objective: To develop a new computer control system for the NIST Standard Reference Photometer (SRP). This system should allow unattended ozone monitor calibrations to be performed in addition to improving the quality assurance of the calibration itself.

Problem: The NIST SRP is the standard for ozone measurements at NIST, for the U.S. EPA, and for an increasing number of other National Laboratories throughout the world. The existing SRP computer control system requires an operator to be present during a calibration run to handle a few minor tasks on an intermittent basis. A typical full calibration procedure of an individual instrument requires three independent calibration runs of approximately three hours each. During this process the operator spends much of the time waiting between measurements. Automation of the now operator dependent steps will decrease time spent on operation of the SRP, and should increase the reproducibility of the measurements, thus improving the quality of the calibration.

Approach: Complete control of the calibration process will be obtained by incorporating the latest technology in analog and digital input/output (I/O) control circuit cards available commercially combined with advanced software development. Generation of a given ozone concentration requires two electrical control signals for the air flow rate and the intensity of ultraviolet (UV) radiation that generates the ozone. These signals, previously controlled by manual adjustment of independent potentiometers, will now also be controlled by two voltage signals from the computer I/O card. A switch configuration on the SRP will allow the manual potentiometer control to remain available if desired. The basic SRP control functions will still be handled by the computer I/O card.

The operator dependent decision of when an ozone sample concentration is stable enough to begin actual data collection will now be automatically determined by statistical analysis of preliminary data, or the passing of a preset time. This same statistical analysis approach will be used to detect instability during the actual data collection.

Finally, all previously encountered commercial ozone monitors have analog output signals that relate to the actual ozone concentration. The computer I/O card will read these signals to acquire the guest instrument concentration values.

Results and Future Plans: During FY95, we designed and developed the main portion of the hardware and software. Necessary hardware changes were made to the NIST backup SRP0 to be used during testing and development. An initial test was set up to demonstrate that control of the SRPs basic functions, air flow, UV radiation intensity, and reading of a guest instrument data were obtainable automatically. The software is now in the stage of debugging and validation; completion is expected early in FY96.

After complete evaluation of the new control system efforts will then be directed toward upgrading all 18 SRPs located throughout the U.S., Canada, and Europe. Additional functions will be added later to allow guest instrument input data to be in IEEE 488, and RS-232 format.

6. ^{14}C Measurements Used to Evaluate Regional Source Apportionment of Air Particulates

***D.B. Klinedinst**, G.A. Klouda, and G.E. Kenniston (Colorado Department of Public Health and Environment)*

Objective: To use radiocarbon (^{14}C) analysis to apportion uniquely and quantitatively the fossil *vs* biogenic carbon sources of the PM10 (<10 μm diameter) carbon aerosol in Denver during episodes when the National Ambient Air Quality Standard (NAAQS) was exceeded.

Problem: On four days during the winter of 1992-93, the Denver metropolitan area failed to meet the NAAQS for PM10 aerosol (150 $\mu g/m^3$ over 24 hours) for the first time since 1987. The state implementation plan to control these aerosols relies on dispersion and chemical mass balance models to estimate residential wood combustion (RWC) carbon contributions to the total PM10 mass. However, for these samples, the two models yielded discrepant results, 10% *vs* 80% RWC, respectively. Consequently, the Denver Regional Air Quality Council and the EPA Region VIII requested that selected samples be submitted to NIST for ^{14}C analysis as an independent means of testing the validity of the modeling results.

Approach: Using techniques developed at NIST for separating small (sub-milligram) quantities of carbon from environmental samples, ten PM10 aerosol samples, collected within the Denver metropolitan area on the four exceedence days, were processed to recover the total carbon fraction. Sample carbon, as CO_2, was then prepared as Fe-C targets with subsequent ^{14}C measurements *via* accelerator mass spectrometry (AMS) at the NSF-Arizona AMS Facility at the University of Arizona. From the ^{14}C results, estimates of RWC were obtained by assuming a two-source model, RWC and motor vehicle (MV) emissions. The RWC component accounted for atmospheric CO_2 assimilated by trees over the typical age of logs burned. The MV component considered the effect of MTBE- and ethanol- blended gasolines.

Results and Future Plans: With one exception, (New Years Day), the ^{14}C derived estimates for the RWC contribution to the total PM10 carbon fell within a narrow range of 12-23%. The two-source model (RWC and MV) is simplified, as there are other potential sources of PM10 carbon in the Denver airshed. Thus, these ^{14}C results represent an upper limit to the RWC contribution for these samples. These results are similar to the dispersion model results and indicate an over prediction of RWC by the chemical mass balance model.

Potential future work includes ^{14}C analysis of selected samples in the proposed Northern Front Range Air Quality Study, tentatively scheduled for the winter of 1996-97. These results will be used to evaluate further the chemical mass balance model approach to apportionment of RWC.

7. *The ^{13}C Composition of Atmospheric CO in Brazil: A Model Scenario to Monitor Biomass Burning*

J.M. Conny, R.M. Verkouteren, and L.A. Currie

Objective: To demonstrate the scope of atmospheric ^{13}CO variation in a region where biomass burning is a major source of CO.

Problem: Different types of CO sources (e.g., fossil-fuel combustion, biomass burning, oxidized vegetative emissions, CH_4 oxidation) have different $^{13}C/^{12}C$ ratios due to isotope fractionation. The isotopic composition of atmospheric CO reflects the flux-weighted isotopic composition of sources as well as fractionation effects of sinks. Hence, ^{13}CO analysis of ambient air is potentially a powerful tool for distinguishing anthropogenic from natural sources of CO in the troposphere. However, to predict where and when to collect ambient air samples for ^{13}CO analysis, *a priori* information is needed on the extent of isotopic variation caused by varying weather conditions and time/space variations of individual source emissions.

Approach: ^{13}C signatures of three CO sources (biomass burning, oxidized vegetative emissions and CH_4 oxidation) were used to calculate tropospheric $^{13}CO/^{12}CO$ ratios at four remote sites in the rainforest and savanna of Brazil during August 1992. The CO contribution from fossil-fuel combustion at each site was considered negligible. A three-dimensional air-mass transport and dispersion model was used to calculate the CO contributions from satellite-detected burn sites. The sites were mainly in the Brazilian savanna where much of the biomass consists of relatively ^{13}C-enriched tropical grasses.

Results and Future Plans: Results suggest that the ^{13}CO compositions at the surface and 1.35 km above the surface for all four sites on 5 August were $-22^0/_{00}$ to $-24^0/_{00}$, close to the ^{13}C composition for CO from biomass burning ($-21.3^0/_{00}$). Therefore, at all sites, ambient ^{13}CO composition was likely affected to a great extent by biomass burning during the first week of August 1992.

Results suggest that on 11 August, three of the four sites were again affected largely by biomass burning. However, at the fourth site in the Amazon basin, the calculated $\delta^{13}CO$ average was $-34^0/_{00}$, $10^0/_{00}$ less than the previous week. At this site, the proportion of CO from ^{13}C-depleted natural sources (e.g., CH_4 oxidation) during the week of 11 August was likely substantially greater than the previous week.

Thus, tropospheric ^{13}CO composition may be highly variable from week-to-week in the Amazon region during the biomass burn season. As a result, estimates of contributions from anthropogenic and natural CO sources may also be highly variable if based on ^{13}CO composition of ambient air collected over the short term.

Future work will focus on further validation of the model and the determination of an average $\delta^{13}C$-value with uncertainty for CO from biomass burning over the entire Brazilian burn season (June-October). This $\delta^{13}C$-value will serve as a ^{13}C signature for emissions from biomass burning in the tropics overall.

8. *Chemical Image Stack Viewing and Scaling in 3-D SIMS Depth Profiling*

D.S. Bright and R.G. Gillen

Objective: To correct three dimensional (3-D) Secondary Ion Mass Spectrometry (SIMS) images for differences in local sputtering rates.

Problem: In 3-D SIMS, a series of elemental secondary ion images are acquired as the sample surface is continually eroded by ion bombardment, generating a "stack" of images with each image corresponding to a slightly greater depth below the sample surface. Figure 1 shows three secondary ion images (evenly spaced sputter-time sequence) of implanted boron in an inconel alloy sample. Processing of these images allows for a 3-D reconstruction of the elemental distribution in the sample with a lateral resolution of <1 micrometer and a depth resolution of ~10 nm. For any 3-D imaging technique based on ion beam sputtering, it is assumed that the erosion process removes material at a uniform rate across the analyzed area. However, for many samples such as this one, the local erosion rate is affected by sample characteristics such as initial surface roughness, chemical composition, and crystallographic orientation. This is seen in Figure 1, where the implant layer is actually at a constant depth, but appears in different grains in different images due to the difference in sputtering rate among grains.

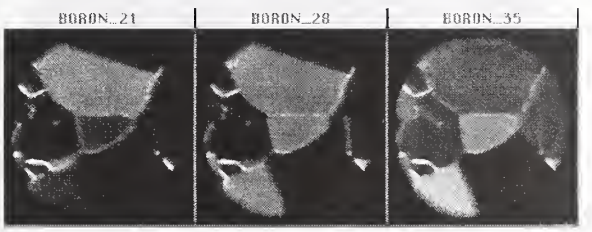


Figure 1. SIMS image of Boron implant at three different depths.

Approach: If the erosion rate at each point in the (2-D) image is known, then the pixels in a given slice can be assigned to the appropriate real physical depth, and the 3-D reconstruction corrected, pixel by pixel, for the varying erosion rate. The erosion rate is determined using ion implantation of a tracer element into the sample which has a peak concentration at a uniform depth throughout the sample. MacLispix, an image processing system developed and used by our research group, was modified to load a series of images as a stack, and manipulate the data for examination and depth correction.

Results and Future Plans: Figure 2 shows an image in the stack and a plot of intensity going down through the stack, for one point selected by a mouse click within the bright grain at the top. Conversely, clicking on the plot (see arrow in Figure 2) displays the image corresponding to that depth. After depth correction, the implant layer appears in all of the grains in the same few images, and the depth plots all have a maximum at the same point (not shown).

Figure 2. One selected image in stack.

In FY96, we plan to test this tool on more data and also use erosion rates measured with an atomic force microscope, which physically measures the crater depth.

Publications:

Gillen, G., Bright, D., Lorincik, J., and Mogren, S. **"Quantitative 3D Image Depth Profiling SIMS: Characterization of Patterned Ion Implants in Silicon,"** in Secondary Ion Mass Spectrometry: SIMS X, John Wiley and Sons, 1995 (in press).

9. *X-Ray Focussing and Defects of Capillary Bundles Measured on the X-Ray Optical Test Bench*

T. Jach, S. Thurgate (Murdoch Univ., Perth, Australia), and E. Steel

Objective: To develop x-ray focusing techniques to increase the intensity available from a conventional x-ray source for microanalysis.

Problem: Developing a focused x-ray beam source would be useful for intermediate resolution (1-100 μm) microanalysis using x-ray fluorescence and diffraction analyses. We are currently assessing various optics that might focus x-rays. One promising method for focusing x-rays is by capillary optics. The fabrication of a capillary bundle depends on the ability to identify defects of alignment and x-ray transmission on a very small scale. These problems have hampered the development of commercial-quality lenses by X-Ray Optical Systems, Inc., an ATP Awardee.

Approach: We have constructed a precision optical bench with a high-resolution magnifying x-ray camera that permits us to obtain images of the transmitted radiation and defects of the capillary bundles. The optical bench allows for the measurement of a large number of samples which represent a wide variety of manufacturing conditions.

Results and Future Plans: During FY95 we identified various defects that occur in capillary bundles as a result of the production process or of degradation that occurs afterward. Figure 1 shows transmission through a compound capillary bundle that contains several types of defect. The bundle is made up of smaller bundles (~50 μm dia.) that are sintered together. Observed defects include: (a) the interface region of the bundles has low transmission; (b) Defective regions exist that impede transmission altogether; (c) Some of the bundles have not fused together properly; (d) Individual capillaries that do not transmit. The smallest feature we are able to identify in this evaluation has a width of about 12 μm.

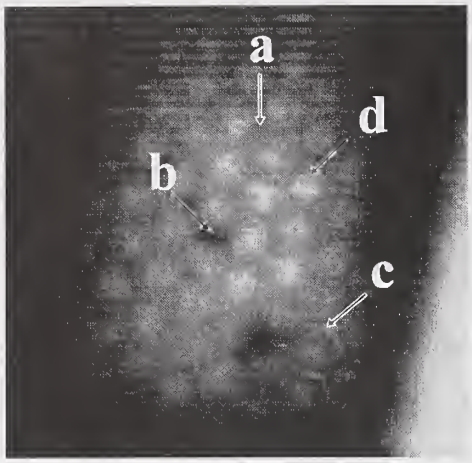


Figure 1. Digital x-ray image showing defects in capillary optic.

Figure 2 shows the effect of a tapered capillary bundle which focusses the x-rays. Figure 2(a) shows the image of the x-rays leaving the bundle, which includes various defects of transmission reducing the efficiency of transmission. Figure 2(b) shows the spot that is obtained at the focal point of the optical element. Even with its attendant defects, the focal spot shows an enhancement factor of about 50 in x-ray intensity for a 130 μm diameter spot. Optimization of the geometry should increase this intensity even more.

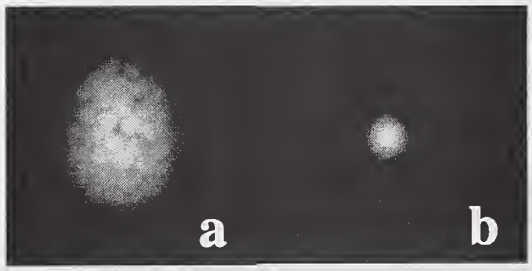


Figure 2. Digital x-ray image of tapered capillary bundle at two focal positions.

We are providing these measurements so that our collaborator, X-Ray Optical Systems, can produce a capillary bundle that is optimized for microanalysis with a rotating anode x-ray tube. We intend to demonstrate the improvement of intensity that can be realized in actual microanalysis and apply it to the analysis of real-world systems. While the enhancements that have already been realized in x-ray intensity are highly significant, the elimination of the defects that we have detected promises considerable improvement.

10. Preparation and Certification of K-411 Glass Microspheres for Electron Probe Microanalysis

R.B. Marinenko, S.V. Roberson, and J.A. Small

Objective: To develop and certify a material of known shape, size, composition, and homogeneity as a research material or a Standard Reference Material (SRM) for the electron probe microanalysis (EPMA) of particles.

Problem: The initial production and electron probe quantitative analysis of glass microspheres in the 1-40 μm diameter range made from K411 glass (NBS SRM 470, Glasses for Microanalysis) was reported by this laboratory in 1989. For certification, a large number of analyses of the microspheres were needed requiring the use of automated techniques, which in turn required a procedure to distribute the spheres on an analysis medium without agglomeration.

Approach: Spheres were prepared from a finely ground suspension of K411 glass shards by heating them to just below the melting temperature (900-1500 °C) in a tube furnace. As the shards traveled in the upward draft of the furnace, spheres formed that were primarily 1-40 μm in diameter. The resulting sample (7 g) was divided into 125 specimen vials for eventual distribution. Eight vials, including duplicate samplings from two vials, were selected at random for quantitative EPMA.

The spheres were distributed for analysis on double-sided conductive carbon tape adhered to a 2.5 cm carbon disk for support. Approximately 150 spheres were be distributed with minimal agglomeration.

The specimens were analyzed with MACLISPIX, a special purpose public domain program developed in this laboratory for a Macintosh computer. Spheres were analyzed in spot mode using an energy dispersive spectrometer (EDS). Spectra were processed and quantified with DTSA, the Desk Top Spectrum Analyzer computer program also developed here. A bulk specimen of SRM 470 (K411 glass) was used as a standard.

Results and Future Plans: Results of the analyses of the ten specimens are compared in the table below with the certified values for the K411 bulk SRM. Oxygen was determined by stoichiometry. The differences between the two results and the larger uncertainties observed for the spheres are attributed to the sphere geometry and small size of some of the spheres. The path length of the x-rays leaving the sphere is decreased compared to that of a flat specimen resulting in decreased x-ray absorption, especially for the low atomic number elements (Mg and Si). Also, the excitation volume of the beam may exceed the size of the smaller particles (1-3 μm) thus adding to the reported uncertainty. Additional specimens are being analyzed to be sure the results lie within uncertainties in the table. Also, a bulk analysis of the microsphere material is planned to determine whether the heating process used in sphere formation causes composition changes.

Comparison of K411 Spheres with Bulk
(Conc. in Wt.%)

Elem.	Bulk SRM Conc.	Uncer-tainty* ±	Spheres Conc.	Uncer-tainty* ±
Mg	8.85	0.12	9.1	1.4
Si	25.38	0.09	25.7	2.2
Ca	11.06	0.14	11.1	2.5
Fe	11.28	0.16	11.2	1.8
O	42.36		42.9	

* Uncertainties for elements are estimates from 2σ values assigned to the oxides in the SRM certificate.
** Uncertainties are pooled 2σ values for the ten samples including within and between specimen standard deviations.

Publications:

Roberson, S. et. al., **Certification of K-411 Glass Microspheres with Electron Probe Microanalysis**, Microbeam Anal. - 1995, VCH Pub. Inc., p. 225.

11. *Relative Peak Intensities of Selected Gold L X-Ray Lines*

R.L. Myklebust and R.B. Marinenko

Objective: The objective of this study was to determine the necessary procedures for measuring the relative line intensities for the L and M x-ray lines using a wavelength dispersive spectrometer (WDS) on an electron probe microanalyzer.

Problem: The relative x-ray line intensities of the K-series lines have been measured by several authors and are considered to be reasonably well known. The L- and M-series lines are less well known and are more difficult to measure due to a number of factors. First, these series include a large number of lines, many of which overlap. Second, multiple absorption edges are associated with each series (three for the L-series and five for the M-series). Third, the relative intensities are affected by multiple ionizations from either direct double ionization or by a radiationless transition (Coster-Kronig transition) to a doubly ionized state. This introduces a variety of small satellite peaks close to the diagram x-ray lines produced by single ionizations.

Approach: The L-lines were measured from pure gold in an electron probe microanalyzer using an energy-dispersive (EDS) detector and a WDS with a LiF analyzing crystal. All WDS data were measured with the second order diffraction to produce better peak resolution at the expense of total intensity. The areas of the x-ray peaks from both EDS and WDS spectra were obtained by the simplex fitting procedure in the Desk Top Spectrum Analyzer (DTSA) program. WDS scans were made of the gold L-series x-ray lines at beam voltages of 13 keV, 14 keV and 25 keV as these voltages are just above the gold L_3, L_2, and L_1 absorption edges, respectively. The absolute efficiency of the WDS system is difficult to determine. However, since we were interested in relative intensities over a limited energy region, the relative efficiency could be calculated by plotting the continuum intensities measured at or near the energies of the x-ray lines. The x-ray continuum measured with the EDS was combined with the WDS continuum measurements to produce the WDS efficiency as a function of energy. The relative efficiency plots for the three beam voltages are similar. The change in efficiency is primarily due to the change in solid angle as the spectrometer is scanned away from the specimen to higher wavelengths (lower energies). The EDS peaks were fitted with a Gaussian peak profile and the WDS peaks were fitted with a combined Gaussian-Lorentzian profile.

Results and Future Plans: The results for the gold lines from the L_3 absorption edge are shown in the table for all of the measurements together with the values currently used in the DTSA program. While it is encouraging that the values obtained are similar, it must be remembered that these are the easiest ones to measure when only the L_3 absorption edge is excited. The fact that the higher voltages also produce similar results is indeed encouraging. We intend to complete the gold measurements and then continue with other selected elements.

Line	WDS			DTSA
Ratio	13 keV	14 keV	25 keV	Data
$L\alpha_1/L\alpha_1$	1.000	1.000	1.000	1.000
$L\alpha_2/L\alpha_1$	0.087	0.114	0.129	0.114
$L\beta_2/L\alpha_1$	0.224	0.200	0.229	0.219
$L\beta_6/L\alpha_1$		0.014	0.019	0.014
$Ll/L\alpha_1$		0.040	0.020	0.056

Publications:

Myklebust, R.L. and Marinenko, R.B., **"A Look at the Relative Peak Intensities of the L X-Ray Lines of Gold"**, Microbeam Analysis-1995, Edgar Etz, Ed., p. 223.

12. *Quality Control Methods for Energy Dispersive X-ray Detectors*

***E.B. Steel**, R.B. Marinenko, R.L. Myklebust, D.E. Newbury, J.A. Small, S. Turner, and B.B. Thorne*

Objective: To develop formalized methods to fulfill quality system requirements for the monitoring of our chemical measurement systems. We initiated this task with one of the most commonly used analytical instruments, the Energy Dispersive X-ray Spectrometer (EDS).

Problem: Formalized quality systems are becoming required throughout industry as well as in research. The various quality standards, such as ISO 9000, Guide 25 and ANSI/NCSL Z540-1, require methods and data for assuring the quality of products. In the microanalysis laboratory chemical measurements are a routine product and many electron-beam microanalysis measurements rely on EDS detectors. Electron Probe Microanalyzers (EPMA), Scanning Electron Microscopes (SEM), and Analytical Transmission Electron Microscopes (AEM) all use EDS detectors to obtain chemical information. Many laboratories performing analyses using EDS on a wide variety of chemical systems have contacted us for help and guidance in developing quality systems.

Approach: We designed the methods to comply with international quality standards and to be applicable to our diverse applications. We chose the quality measurements that would be useful for monitoring the major chemical measurement functions of the EDS systems. The EDS and instrument parameters that we monitor include detector resolution, detector sensitivity, energy calibration, peak to background, dead time, and electron beam voltage (on the EPMA and SEM).

We chose materials that would allow us to measure these parameters reproducibly and provide traceability to our national standards system. Several criteria were used in choosing the material. For all analytical systems the material has to be stable over long periods of time (years) so that control charts can be used. Preferably sample preparation artifacts are minimized or absent, so that when it is necessary to re-prepare the material, the new results will be directly comparable to previous analyses. For example, the EPMA/SEM material had to be conducting so that EDS measurements, such as low energy efficiency, would not be affected by the carbon or other conductive coating or specimen charging. The material must yield major x-ray peaks so that statistically significant peaks can be collected efficiently. These peaks must occur over a broad range of energies so that EDS parameters, which are a function of energy, can be calculated and monitored. The concentrations of the elements should be known and homogeneous across the whole specimen; if possible, the material should be an SRM that is certified for the parameters of interest or traceable to such an SRM.

Results and Future Plans: We chose two SRMs for these measurements: the 60% Au 40% Cu wire from SRM 482 Gold-Copper Wires for Microprobe Analysis for the SEM and EPMA and SRM 2063a Microanalysis Thin Film Mg-Si-Ca-Fe-O for the AEM. These materials meet the criteria listed. A standard operating procedure was designed and implemented that defined the data acquisition and instrument parameters such as electron beam voltage, current, collection live time, specimen-detector geometry, pulse-height analyzer settings, etc.

The procedure has been implemented and data are being collected over a long time period to determine the best primary factors for control charts. We are using NIST's Desktop Spectrum Analyzer (DTSA) to measure and determine the quality control factors. Control limits for the control charts are being investigated based on the measurement reproducibility and the chemical measurement requirements of the techniques. We will compare the results and capabilities of DTSA to those from existing x-ray analyzers so that a robust quality control method can be made that will assist comparison across many labs and instruments. When this is completed a method will be made available to the community.

13. *Automated Scanning Electron Microscopy: Detection Limits for Particle Populations*

J.A. Small

Objective: To provide accurate particle analyses and groupings based on elemental compositions from automated scanning electron microscopy (ASEM) analysis of large numbers of particles.

Problem: When applied to the automated analysis of large numbers of particles, the scanning electron microscope is used as a macroanalytical instrument. This is accomplished by combining the individual SEM analyses from all the particles and grouping the data to infer sample or population characteristics. In an effort to analyze as many particles as possible, ASEM x-ray analysis employs short x-ray counting times, typically between 0.1-30 s. In comparison, the counting time used in conventional electron probe analysis of bulk materials is often on the order of 2-5 minutes per sample. One difficulty associated with this approach is that the short analysis times may reduce the detection limits for trace ($\leq$ 0.01 wt. fraction) elemental constituents. These elements in turn may be critical to the identification of a given particle grouping.

Approach: Trace element detection was studied by analyzing two sets of glass shards in the 1-10 μm size range. One set of shards contained 0.007 Wt. fraction Fe and the other set contained no Fe in a similar matrix. Thirty particles from each glass were analyzed for three different counting times 15, 60, and 200 seconds. The results were used to test and compare different analytical procedures for trace-element detection.

Results and Future Plans: Two different methods were studied for trace-element detection. One method, used for qualitative analysis in the DTSA x-ray analysis program, involved the processing of the spectra with a modified zero-area top-hat filter and comparing peak integrals to background integrals. The second method, used for quantitative analysis in DTSA, involved multi-linear-least-squares (MLSQ) fitting of the spectra processed with a Savitzky-Golay zero-area top-hat filter. Fe concentrations were then determined by comparison to a standard.

The results are expressed as either false negative or false positives. False negatives and positives for the qualitative procedure are spectra in which the Fe peak was not found in the Fe glass or was found in the non-Fe glass. In the case of the quantitative procedure, false negatives were spectra from the Fe-containing glass in which the Fe concentration was below a 95/95 one-sided tolerance limit calculated from the non-Fe containing glass particles. False positives for the quantitative procedure included the spectra from the non-Fe glass particles in which the Fe concentration was above a 95/95 one-sided tolerance limit calculated from the Fe-containing glass particles.

Overall the number of false negatives obtained from the qualitative procedure is very high. However there is a marked reduction with increased analysis time. With the qualitative procedure, Fe was missed in 90% of the 15 s spectra, 67% of the 60 s spectra and 20% of the 200 s spectra. False positives were detected with the qualitative procedure in 6.7% of the 15 s spectra, 13% of the 60 s spectra, and 20% of the 200 s spectra. In the quantitative procedure Fe was missed in only 3% of the 15 s spectra and 0% of the 60 and 200 s spectra. There were no false positives in the MLSQ procedure.

These results suggest that if particle grouping is based on the detection of trace elements, with concentrations at a percent or less, then the MLSQ procedure provides an accurate and robust method for trace-element detection even at analysis times as short as 15 s.

Future work on the ASEM analysis of particles will include the development and introduction of advanced methods for the quantitative analysis of particle x-ray spectra. Improving the quantitative analysis of individual particles will enable us to better define particle groups and provide a more accurate sample analysis from ASEM data.

14. *New Design for a Low Magnification Detector in the Environmental Scanning Electron Microscope*

S.A. Wight *and M.E. Taylor (Univ. of Maryland)*

Objective: To develop a device to facilitate low magnification imaging in an environmental scanning electron microscope (ESEM).

Problem: Current design of our environmental scanning electron microscope (ESEM) provides for a low magnification of only 200x. Decreasing this value to magnifications <100x would provide increased ease in locating structures, particles, or areas of interest on a given sample for imaging or elemental analysis. The lower magnification also allows larger spatial relationships to be observed and investigated.

Approach: Several modifications of the various components in the final optical element of the ESEM were tried to lower the magnification: increasing the bore opening; modifying the set distance; and a combination of these two modifications.

Results and Future Plans: Following experiments that changed the diameter of the final beam aperture and tested a second limiting aperture, we arrived at an optimal design. The final stationary aperture was replaced with a variable aperture, much like the diaphragm apertures used in cameras and light microscopes. The aperture can be opened wide for low magnification imaging and then closed down for high magnification imaging where it will not restrict the scanned beam. The aperture can be changed by using a micromanipulator, without the need to break the sample vacuum. The variable aperture, low magnification device performed well in low (~20-30x) and high magnification imaging. A patent application has been approved for these modifications.

Future plans include adding another pumping zone to the area created between the new pressure limiting aperture and the variable aperture.

Publications:

S.A. Wight, M.E. Taylor: "An Approach to Improve Low Magnification Imaging in the Environmental SEM", Conf. Proc: Microbeam Analysis-1995, p. 391.

M.E. Taylor: U.S. Patent No. 5485008, Jan. 16, 1996.

15. *Femtochemistry at Surfaces Using Tunnel Junctions*

J.W. Gadzuk

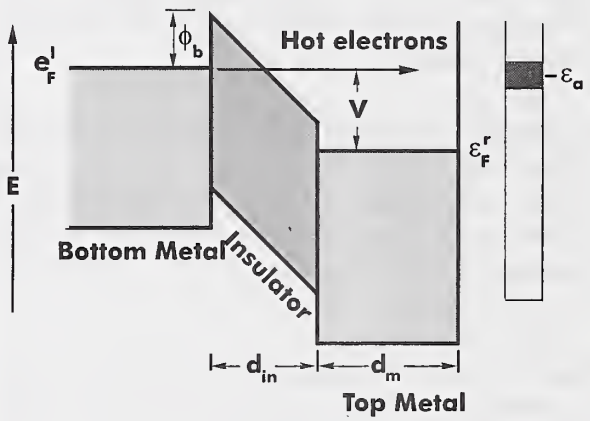
Objective: Develop novel, non-thermal methods for controlled atomic-level manipulation and chemical processing at solid surfaces.

Problem: A promising realization of Femtochemistry, based on inelastic resonant scattering of hot electrons by the reactants, achieves control of the intra-molecular dynamics required for select chemical processes. This is accomplished by controlling, in an appropriate way, the energy distribution of the hot-electron flux upon the surface. The major technical challenges are twofold. First, a useful theoretical model for the process must be developed that provides the causal relationships between a desired chemical output and the characteristics of the incident, hot-electron distribution. Second, lab systems capable of producing the required hot electron distributions must be realistically attainable.

Approach: The theoretical foundations for two radically different methods of electron control have been developed. The first method utilizes an energetic broadband distribution of hot electrons, ubiquitous to most current laser-excited surface experiments. The second method is based on a novel application of a solid state metal-insulator-metal tunnel junction to produce a monochromatic, tunable electron flux internally incident upon the top metal-vacuum surface where the controlled Surface Femtochemistry occurs *via* scattering through the adsorbate negative ion resonance state near ε_a, as shown in Figure 1.

Results and Future Plans: The relevant theory for the tunnel junction device has been developed in terms of an independent 4-step model: I) field emission tunneling from bottom metal to tilted insulator conduction band; ii) transport through insulator, with possible phonon/polaron losses; iii) hot electron transport and attenuation across top metal film; iv) resonant inelastic hot electron scattering from adsorbate/reactant. The theory of each independent step has already been worked out. The present work has, for the first time, provided a motivation for unifying these components to produce a controlled femtochemical device. Theoretical expressions for reaction rates (e.g., selective bond breaking dissociation or desorption rates) as a function of applied voltage have been obtained which provide predictive capabilities. By appropriate choice of device parameters ϕ_b, d_{in}, and d_m and the top metal species, one can produce an electron source optimally suited for a particular femtochemical process, as determined by the energetic placement of ε_a. This novel aspect has been emphasized in the reported studies.

In FY96, the use of the tunnel junction femtochemical device will be studied to investigate reactive processes beyond elementary selective bond breaking. Other novel applications of this emerging new technology will be sought.



16. *Femtosecond Laser-Induced Surface Reactions: Testing Theoretically Predicted Population Distributions with State-Resolved Diagnostics*

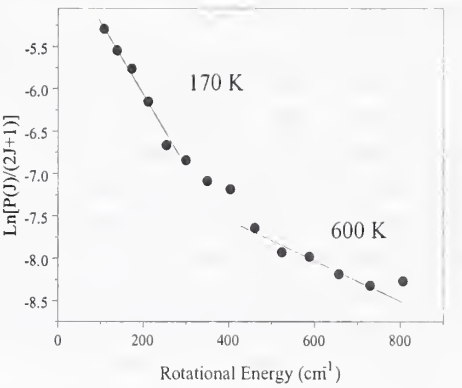
***L.M. Struck**, S.A. Buntin, L.J. Richter, R.R. Cavanagh, and J.C. Stephenson (PL)*

Objectives: Test state-of-the-art theoretical predictions of the internal state populations that arise from femtosecond laser induced desorption of CO from Cu(100).

Problem: Laser-induced desorption of molecules from well-characterized surfaces has served as a test bed for a variety of theoretical and experimental probes of surface dynamics. With the recent development of molecular orbital-based theories of the dynamical coupling between adsorbates and surface electronic excitations, it has become possible to predict the details of certain laser stimulated chemical events. However, there have been no laboratory measurements that could establish the quantitative accuracy of these theoretical predictions.

Approach: Theoretical predictions have been made for the disposition of energy in CO when femtosecond laser pulses are used to desorb it from a Cu(100) surface. We have undertaken a series of measurements to characterize this CO desorption process. Since the theory predicts the population of internal states for the CO desorbed in this process, and a yield that scales as the pulse energy raised to the fifth power, we have undertaken an effort to characterize both of these factors. To establish the dependence on peak power, we have used 400 nm pulses ranging from 100 to 300 fs in duration, with peak energy densities near 100 $\mu J/mm^2$. State-resolved measurements are acquired utilizing REMPI detection of the desorbed CO.

Results and Future Plans: Preliminary results suggest a yield that scales as laser fluence to the seventh power, in rough accord with the theoretical prediction. The v=1/v=0 vibrational state populations show a comparable agreement with theory, suggesting T_{vib} for the desorbed CO of over 1000 K. However, the translational and rotational degrees of freedom do not provide strong support for the theoretical effort. In the case of the rotational states, a single temperature cannot fit the data. The population of rotational states is suggestive of two temperatures, the colder component is in good agreement with the theoretical prediction, while the second component is about a factor of three hotter. The kinetic energy distribution is noteworthy, being approximately a factor of three colder than the theoretical prediction.



Work is continuing on this test of theory. Our primary focus is to establish better control of the laser energy density, as current data have revealed that the desorption yield is sensitive to subtle changes in pulse duration and spatial profiles. The reproducibility of these factors will be essential to a valid test of the remaining theoretical predictions and to the separation of the two channels that appear in the rotational distribution.

Current discussions with theorists who have provided these predictions are expected to lead to refined models of the underlying energy transfer processes that are characteristic of this system.

17. *Liquid Crystal Alignment Layers: Non-destructive Determination of Ordering with Non-linear Optical Spectroscopy*

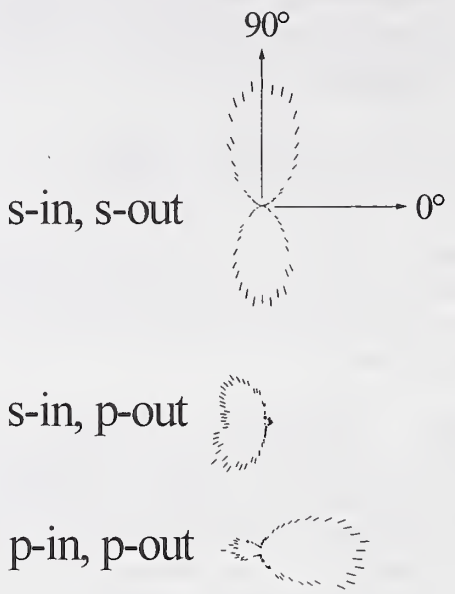
L.J. Richter, K.W. Kolasinski, J.C. Stephenson (PL), and W.M. Gibbons (Alliant Techsystems Inc., Wilmington DE)

Objective: Develop non-destructive, optical probes of substrate characteristics relevant to the alignment of liquid crystal adsorbates.

Problem: The fabrication of liquid crystal displays currently involves the empirically optimized mechanical preparation of a polymeric substrate to induce alignment in a contacting liquid crystal. Optimization and control of the preparation of these alignment layers is significantly hampered by the absence of both non-destructive diagnostics of the prepared layer and a fundamental understanding of the liquid crystal/alignment layer interaction.

Approach: In centrosymmetric media, second harmonic generation (SHG) is symmetry forbidden, imparting extreme surface sensitivity to this nonlinear optical (NLO) technique. Additionally, SHG is more sensitive to interface structure than linear optical techniques by virtue of the transformation properties of the relevant mixing coefficients. SHG has been employed by various researchers to study adsorbed liquid crystal (LQ) monolayers on mechanically processed substrates with great success. There are essentially no reports in the literature of SHG studies of the LQ alignment layers in the absence of LQ monolayers. Characterization of the alignment layer itself should lead to a greater understanding of the fundamental interactions important to LQ assembly, and possibly result in a useful analytic tool for the processing of LQ films.

Results and Future Plans: SHG studies were performed on LQ alignment layers consisting of a thin film of polyimide copolymer doped with a dye to enhance the SHG response. Shown in the figure is the second harmonic at 532 nm detected following 1064 nm irradiation of a heavily buffed sample as a function of the orientation of the buffing direction with respect to the plane-of-incidence and the 532 nm and 1064 nm polarizations. The data are presented as polar plots.



Clearly the SHG technique has adequate sensitivity for the characterization of alignment layers containing dye dopants. Analysis of the SHG data establishes that the layer has C_s symmetry, i.e., the buffing not only establishes a preferred alignment, but actually orients the film. Additional studies on a series of films with varying degrees of buffing are underway to correlate quantitatively the asymmetry of the alignment layers with their ability to align LQ films.

Additional studies will be performed to attempt to extend the technique to alignment layers that do not contain dye dopants, and to refine quantitative models of the SHG response.

18. H_2 Plasma Processing of GaAs Surfaces for Oxide Thin-film Growth

S.W. Robey

Objective: The primary objective was to investigate aspects of the growth of MgO buffer layers on GaAs and to develop alternative methods for preparing GaAs surfaces for MgO growth. This is a first step towards allowing the integration of ferroelectric and non-linear optical oxides with GaAs.

Problem: The integration of thin films of ferroelectric, high T_c, and non-linear oxides with semiconductors such as GaAs and Si is desirable for a variety of microwave and optoelectronic applications. However, typical semiconductor processing procedures can be difficult to incorporate into the oxide growth. GaAs processing requires the removal of native oxides and production of a smooth surface prior to thin-film growth. An AlGaAs layers, is achieved by high temperature annealing in an As overpressure to suppress surface roughening. In the case of oxide thin-film growth, it would be useful to have simpler surface preparation methods that do not require an elevated As background. A number of methods have been explored for producing smooth, clean starting surfaces, but they generally require processing in an additional GaAs MBE system and/or are difficult to control.

Approach: Work by Choquette, *et al.*[1] suggested that chemically-assisted etching using H_2 plasmas could be employed to prepare GaAs surfaces for AlGaAs growth. Building on that work, *in situ* surface analysis techniques (RHEED, Auger spectroscopy) were employed to investigate the growth of MgO on H_2 plasma etched GaAs (001) surfaces and provide information on how this low temperature alternative for removing native oxides influences the quality of the MgO film.

Results and Future Plans: Using an RF excited remote plasma source, GaAs native oxide removal can be achieved at temperatures of approximately 600 K, instead of the 900 - 1000 K that is typically required without the chemical assistance of the H_2 plasma. A subsequent anneal to 800 K can be used to produce a well-ordered As-deficient 4x2 reconstructed surface, although it is not clear that this significantly enhances subsequent MgO growth. *Ex situ* AFM measurements indicate that this process results in only a small increase in surface roughness, with a rms roughness of typically about 0.5 - 0.8 nm over 1 square micrometer after processing. Subsequent deposition of MgO produced films with a MgO(001) orientation normal to the film surface and good in-plane epitaxy with MgO(100)||GaAs (110). This method of surface preparation appears to be as effective for well-oriented MgO growth as more complicated procedures (for instance homoepitaxy of GaAs followed by Sb capping) employed previously.

We also investigated competing reactions that influence the growth of MgO on GaAs when using reactive deposition of Mg in an O_2 background. It was found that at low O_2 pressures, another phase, probably consisting of a Mg-Ga compound, forms which severely inhibits the growth of oriented MgO. The formation of this phase can be suppressed by growth at elevated substrate temperature and O_2 pressure.

Although the starting surface is smooth and MgO can be grown with good normal and in-plane orientations, the growth mode occurs by formation of 3-dimensional islands. This results in a film with significant surface roughness that will probably be unsuitable for optical applications. Future work may be directed towards graded films starting with SrO to CaO to MgO for better lattice match and, potentially, smoother film growth.

Publications:

Choquette, K.D. *et al.*, J. Appl. Phys. 73, 2035 (1993).

19. *Infrared Probes of Reactions on Silicon Surfaces: Oxidation with Water*

L.M. Struck , J. Eng, Jr., B.E. Bent, G.W. Flynn (Columbia University) Y.J. Chabal, A.E. White, S. Christman, E.E. Chaban, K. Raghavachari (AT&T Bell Laboratories), G.P. Williams (Brookhaven National Laboratory), K. Radermacher, and S. Mantl (Institut für Schicht und Ionentechnik, Forschungszentrum Jülich, Jülich, Germany).

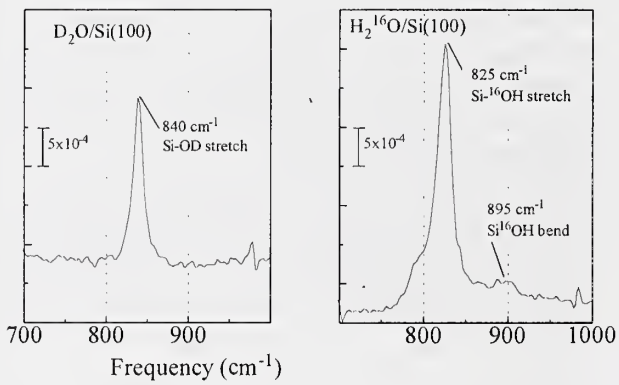
Objectives: Establish infrared spectroscopic measurement technologies for silicon surfaces in the near- to far-IR region, and characterize silicon surface chemistry and spectroscopy in this region.

Problem: The characterization and control of chemical reactions on silicon surfaces is important to semiconductor processing technology. Infrared (IR) spectroscopy has contributed considerably to the characterization of hydrogen-terminated silicon surfaces. However, the IR technique utilized for these studies, multiple internal reflection spectroscopy (MIRS), is limited to frequency regions above 1500 cm^{-1}; therefore, vibrations of Si-O, Si-C, Si-N, and heavier atoms cannot be studied by MIRS. The technique used in the present experiments utilizes a buried layer of cobalt disilicide in single-crystal silicon making single external reflection IR spectroscopy of the silicon surface possible, which allows access to a broad frequency range while maintaining surface sensitivity. We have utilized this technique to study the oxidation of silicon with water.

Given the importance of assigning vibrational spectra in efforts to gain new insights into surface mechanisms, we focused our efforts on a puzzling isotopic shift, first evident during an EELS study over 10 years ago for the Si-OH stretch frequency resulting from water adsorption.

Approach: Infrared spectra are obtained, using conventional FTIR or synchrotron light source, *via* single reflection from a buried layer of $CoSi_2$ in single-crystal silicon. Samples are prepared by 100-200 keV Co^+ ion implantation into silicon with subsequent heating to ~1270 K. The quality of the resulting silicon surface after preparation and cleaning is found to be comparable to unimplanted Si, based on the width of the Si-H stretch vibrational mode as a measure of the surface homogeneity.

Results and Future Plans: The IR absorption spectra show strong vibrational features at 825 cm^{-1} and 840 cm^{-1} after H_2O and D_2O exposures to Si(100), and are assigned to the Si-OH and Si-OD stretch mode, respectively. This apparent frequency shift to *higher* frequency of the Si-OH stretch (820 cm^{-1}) to the deuterated Si-OD stretch (840 cm^{-1}) had puzzled prior researchers. A weak feature at 895 cm^{-1} is assigned as the SiOH bend. IR spectra using $H_2{}^{18}O$ were also obtained to complete the vibrational assignments. The frequency shifts and intensity changes are in excellent quantitative agreement with *ab initio* quantum cluster calculations performed by Raghavachari in this collaborative work. These results establish coupling between the Si-OH stretch and Si-O-H bend vibrations which causes the anomalous frequency shifts and intensity changes.



Publications:

Struck, L.M., Eng, Jr., J., Bent, B.E., Chabal, Y.J., Williams, G.P., White, A.E.,Christman, S., Chaban, E.E., Raghavachari, K., Flynn, G.W., Radermacher, K., and Mantl, S., Mat. Res. Soc.Symp. Proc. 386, 395-400 (1995).

20. *Secondary Ion Mass Spectroscopy Characterization of SrS:(Eu, Sm) Thin Films*

P.H. Chi, D.S. Simons, T.J. Hsieh (Optex Corp.), and D.T. Brower (Optex Corp.)

Objective: To characterize the impurity and charge compensator concentrations in SrS:(Eu,Sm) films produced by electron beam evaporation (EBE) and RF magnetron sputtering (RFMS).

Problem: SrS films form the active layer for the ETOM (Electron Trapping Optical Memory) family of data storage media, an emerging erasable media based on the phenomenon of electron trapping. The ideal SrS films must be free of crystalline defects, have uniform concentrations of dopants (Eu, Sm) and charge compensators (Li, F), and contain low levels of unintended impurities to provide adequate device performance.

Approach: The SIMS technique was chosen for this investigation because of its depth profiling capability, versatility, sensitivity, and accuracy. The SrS:(Eu,Sm) films were deposited on soda-lime glass substrates by the EBE and RFMS techniques. Because the thin films and substrates are non-conductive, a substantial positive charge builds up during the SIMS analysis that may distort the concentration profile. To overcome this charging problem, we gold-coated the sample and used an incidence electron beam during the depth profiling to neutralize the charging while maintaining high sensitivity and accuracy of the measurement.

Results and Future Plans: Figures 1 and 2 summarize the SIMS depth profiles in the EBE and RFMS films, respectively. The Li, O, and F concentrations fluctuated significantly in the EBE-deposited film. We have found that these oscillations are a result of the movement of the electron beam raster pattern during the deposition process. LiF has a high vapor pressure, and thus it is preferentially evaporated from the target surface at a much faster rate than the host SrS. Over time the composition of fluorine was depleted in this region of the target and the concentration decreased in the growing film. When the raster position was moved to erode a new region of the target, the process of preferential evaporation was repeated. No charge compensators were intentionally added to the RFMS target and, as a result, no Li and F concentrations above the background level are detected (Figure 2). Both films show that Na and Al, constituents in the glass substrate, diffuse into the thin film layers. Future investigations will concentrate on methods to block the diffusion process and to purify the raw powders.

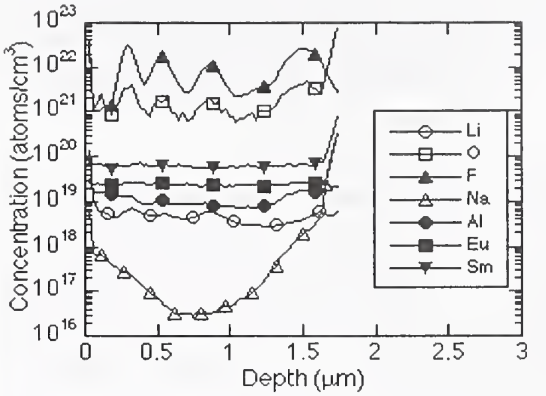


Figure 1. SIMS depth profiles in EBE SrS film

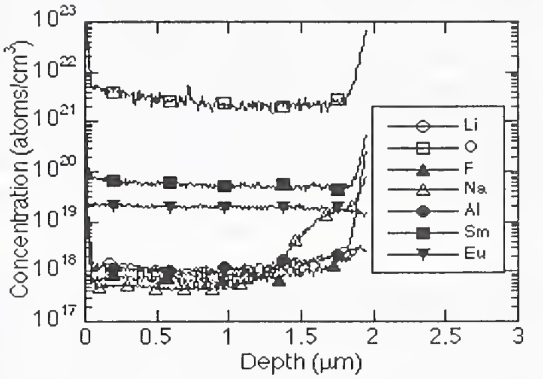


Figure 2. SIMS depth profiles in RFMS film

Publications:

Hsieh, T.J., Revay, R., Brower, D., Chi, P.H., Simons, D.S., Newbury, D.E., and Robey, S.W., **Microstructure and characterization of electron-trapping stimulable phosphor SrS:(Eu,Sm) thin film on glass**, J. Vac. Sci. Technol. A13 (1995) 2732-2738.

21. *Phase Identification of Yttria-Stabilized Zirconia Powders and Coatings By Near-IR FT-Raman Microspectroscopy*

E.S. Etz, L.E. Narváez (Centro Nacional de Metrologia [CENAM], Mexico), and E.B. Steel

Objective: To examine the phase composition of yttria-stabilized powders and coatings by near-infrared excited FT-Raman microspectroscopy.

Problem: Stabilized zirconia, ZrO_2 (typically stabilized by 3 - 8 wt% Y_2O_3), is a broadly useful technological material. Applications involve the fabrication of thermal-barrier coatings produced by various spray coating methods. Control of the microstructure and phase compositions for the zirconia powders and the resultant coatings is of great importance to the final performance properties, such as thermal conductivity and expansion, micro-porosity and adhesion.

Several research groups at NIST collaborate with industrial companies to optimize the processes for deposition of zirconia coatings on various substrate materials. NIST support consists of the physical and chemical characterization of these powders and coatings, whereby information on phase composition is obtained by the bulk methods of x-ray (XRD) and neutron diffraction analysis (NDA). Micro-Raman spectroscopy is used as a third structure-specific analytical method to support the XRD and NDA results and to add the further advantages of spatially resolved micro-sampling, to shed light on any heterogeneity of the samples under study.

Approach: A series of (unstabilized) zirconia powders, consisting of the three polymorphic forms [monoclinic (m), tetragonal (t), and cubic (c)] were analyzed in the FT-Raman microscope to obtain their "reference" Raman spectra, each phase-specific (Figure1). A set of Y_2O_3-stabilized zirconia powders, several of which were used for the preparation of zirconia coatings, were similarly analyzed for phase identity and possible heterogeneity on the micrometer scale (Figure 2). Finally, a number of finished coatings were analyzed, both as planar sections and as cross sections.

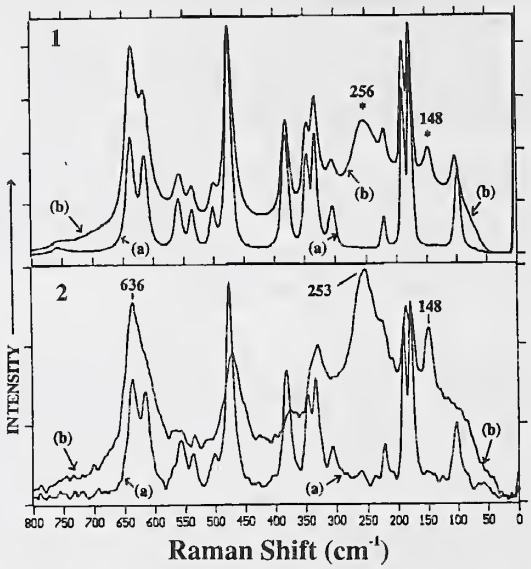


Figure1. Macro-FT/Raman spectra of (a) monoclinic ZrO_2 powder (unstabilized), and (b) mixed-phase monoclinic/tetragonal stabilized ZrO_2 powder (8 wt% Y_2O_3, Sample A).

Figure 2. Micro-FT/Raman spectra showing phase inhomogeneity of feedstock zirconia powder (Sample A) for two microparticles: (a) Particle 1 (size: 43 μm), monoclinic ZrO_2, and (b) Particle 2 (size: 28 μm), mainly tetragonal material.

Results and Discussion: The different phases of ZrO_2 exhibit unique Raman spectra, though they have several features in common (Figure 1). None of the source powders used for coatings contained the cubic phase. Bands distinguishing the two principal phases are at 182 and 193 cm^{-1} (monoclinic) and at ~148 and ~260 cm^{-1} (tetragonal). At this time, a quantification of these phase compositions by Raman spectroscopy is not possible. In macro-measurements, most of the powders show little variability for any given mixed (m-t) composition. In micro-measurements on single particles, significant inhomogeneity is revealed with a range of nearly pure-phase to mixed-phase (m-t) compositions. The spectra of the zirconia coatings all show a pronounced luminescence background upon which is detected, in favorable cases, the expected tetragonal phase. Our results show some discrepancies with the data from the XRD/NDA studies, and these need to be addressed in future work.

22. *The NIST Scanning Scattering Microscope for Surface Microtopography and Defect Characterization*

J. Fine, R.L. King, and J. Lorincik (Czech Academy of Sciences, Prague)

Objective: To develop an advanced, highly sensitive Scanning Scattering Microscope (SSM) capable of producing two-dimensional maps of surface microtopography and defect structure with nanometer roughness sensitivity and micrometer lateral resolution.

Problem: Non-contact optical techniques can provide a very attractive method for the characterization of surface topography. It is known that static optical scattering techniques can detect surface roughness of a few nanometers. The NIST-invented SSM combines this high degree of roughness sensitivity with a scanned, microfocused laser beam to make maps of variations in surface topography. To assess the various advantages of this scanned technique, an advanced high-resolution SSM was developed.

Approach: The surface roughness images obtained with the original prototype SSM indicated the practical usefulness of this approach for mapping defect structures. A new SSM instrument was designed to evaluate fully the capabilities of the technique. This new design concentrated on achieving improved roughness sensitivity, better lateral resolution, and faster data acquisition times.

Results and Future Plans: An advanced working SSM instrument has been developed using current optical and scanning techniques. This design incorporated a computer-controlled, encoded piezo-stage for sample scanning and rapid data acquisition as well as a stabilized He-Ne laser focused to produce a diffraction-limited spot. The new instrument also makes use of a tele-microscope and video camera to facilitate sample changing and alignment. The capabilities demonstrated by this advanced SSM include (1) surface roughness sensitivity of 1 nm, (2) lateral resolution of 5 μm, (3) scan linearity better than 1 μm, (4) laser stability of 0.1%, (5) simplified technique for sample positioning and focusing, and (6) visual microscope imaging of the area of interest. This SSM is probably the most sensitive optical scattering instrument at the present time.

Measurements were initiated on the relationship between defect size and scattered light intensity - a subject of high interest to the microelectronics community. Using a very sensitive atomic force microscope to determine defect size, we were able to measure the scattered light intensity of various sub-micrometer size defects. Realizing that defects produced on insulator surfaces by bombardment with multi-charged ions are very symmetric and of nearly constant size, we will continue in FY96 our intensity *vs* size measurements on these well defined defects. In FY96 we plan to extend our investigation of defect structures at surfaces to those at buried interfaces. We will also study where non-contact optical techniques can be useful, initially using the SiO_2-on-Si system.

Publications:

Fine, J. and Marton, D., **United States Patent Number 4954722,** (Sept. 4, 1990).

23. *Laser Microprobe Mass Analysis of Particles Collected from a Laminar Diffusion Flame*

R.A. Fletcher, R.A. Dobbins (Brown Univ.) and W. Lu (Brown Univ.)

Objective: To determine the chemical composition of particles collected in nanogram quantities from regions of a laminar diffusion flame.

Problem: Research to study gas-to-particle conversion and the subsequent aerosol evolution occurring in or above flames is important for providing fundamental understanding of the flame combustion processes and developing control strategies to limit combustion products relevant to health and environmental concerns. Laser microprobe mass spectrometry and transmission electron microscopy (TEM) have been applied to particles collected in the flame to characterize particle chemical composition and morphology.

Approach: Thermophoretic sampling was used to collect particles onto plasma-etched transmission electron microscope (TEM) grids from a laminar diffusion ethene flame at heights (20, 30, 40, 50 and 70 mm) above the gas burner. TEM images of the precursor particles obtained low in the flame (20 and 30 mm) have the appearance of individual spherules, approximately 5 nm in diameter and have low electron beam opacity. Particles collected at higher regions in the flame show classic soot aggregation and exhibit higher opacity with respect to the transmitted electron beam. To learn more about the chemical composition of these two types of particles, a commercial laser microprobe mass spectrometer having transmission geometry with respect to the laser beam is used in a defocused mode to obtain characteristic mass spectra and to identify differences in chemical species (Dobbins *et al.* 1995).

Results and Future Plans: The positive ion mass spectra of the precursor particles collected low in the flame are characteristic of mid-mass range polycyclic aromatic hydrocarbons (m/z 202 to 302). These masses coincide with the masses of stabilomers predicted to be most favored from chemical thermodynamics. The hydrogen mole fraction, defined in Figure 1, for the precursors is 0.36. Spectra of particles collected high in the flame contain primarily the carbon cluster series, $C_mH_n^+$ where m = 1 to 15 and n = 0 to 2, characteristic of carbonaceous material devoid to a large extent of hydrogen. The hydrogen mole fraction based on peak areas corrected for ^{13}C abundance is 0.15. The results of our experiments suggest that PAH or PAH-like compounds are formed low in the flame and contribute to the composition of the precursor particles. As the small particles are processed at higher temperatures in the upper regions of the flame, hydrogen is lost (see Figure 1) and the precursor particles are transformed into a more carbonaceous aggregate material.

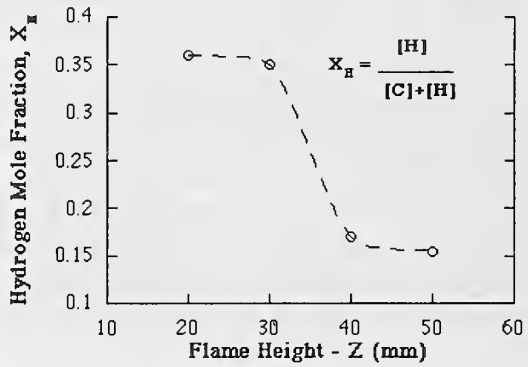


Figure 1. Plot of hydrogen mole fraction as it relates to sampling position in the flame.

Future efforts will be directed to analyzing particles collected between 20 and 30 mm height and to find the source of high mass carbon clusters having m/z >400 and extending out to 3000 including fullerenes which appear to be present in some of the 50 mm samples.

Publications:

Dobbins, R.A., Fletcher, R.A., and Lu, W., **"Laser Microprobe Analysis of Soot Precursor Particles and Carbonaceous Soot,"** Combustion and Flame 100 (1995) 301-309.

24. *SIMS Analysis of DNA Probes on Metal Surfaces*

***R.G. Gillen** and M.J. Tarlov* (836)

Objective: To use Secondary Ion Mass Spectrometry (SIMS) for the characterization of oligonucleotide probe arrays immobolized on gold surfaces.

Problem: One of the most promising new approaches for low cost, high speed DNA sequencing is the DNA "chip". These devices consist of a two dimensional array of immobilized synthetic oligonucleotide probes on the surface of a sensor. Because of the natural base pairing property of DNA, a specific probe in an array will bond or hybridize to an unknown sample of DNA only if the complementary sequence of bases is present in the unknown. Concurrent with the development of these devices, new methods of chemical detection are required. These techniques must have sufficient sensitivity for identification and chemical characterization of oligonucloetide molecules in individual array elements with spatial dimensions of a few tens of micrometers and a depth of single monolayer.

Approach: We have used SIMS for the characterization of oligonucleotide probes that were derivatized with an alkanethiol linking agent and covalently attached to gold surfaces. For spatially resolved analysis, model probe arrays were fabricated using ion beam patterning methods developed previously.

Results and Future Plans: Figure 1 shows a negative secondary ion mass spectrum of a single monolayer of a 25 nucleotide DNA probe containing each of the 4 bases: adenine (A), cytosine (C), thymine (T) and guanine (G), immobilized on a gold substrate. We observe a number of characteristic phosphate-containing ions which indicate the presence of DNA (phosphate ions originate from the DNA backbone) as well as specific parent molecular ions $(M-H)^-$ for each of the four bases contained in the probe. The relative intensities of the nucleotide parent ions may allow us to determine the composition of the probe. We also obtain sufficient intensity from these species to generate molecular ion images. Figure 2 shows two SIMS images of an oligoneucleotide array on gold consisting of a complementary pattern of two oligonucleotide monolayers, one containing 25 cytosines, the other 25 thymines.

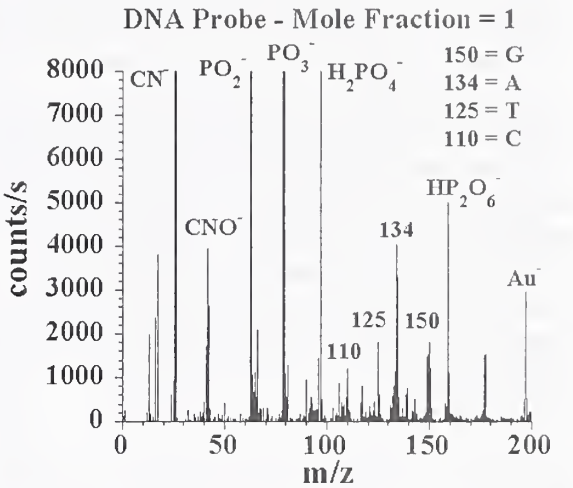


Figure 1. Mass Spectrum of DNA Probe.

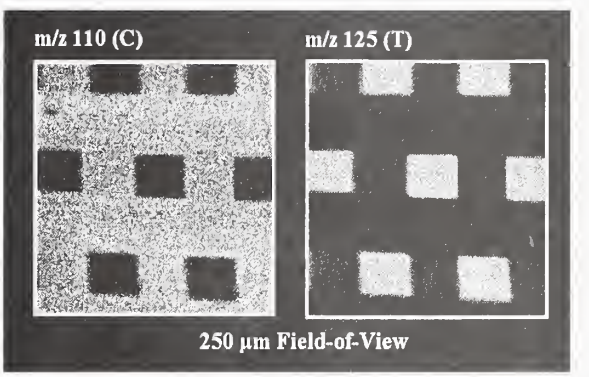


Figure 2. SIMS Image of DNA Probe Array

In FY96 we plan to conduct SIMS analysis on ^{32}P-labeled probe samples to correlate the observed SIMS signal intensities with the absolute surface coverage of the DNA probe. We will also attempt to use SIMS to monitor quantitatively the extent of hybridization in a specified array element.

Publications:

Gillen, G., Roberson, S., Herne, T., and Tarlov, M. **"SIMS Characterization of Patterned DNA Probes on Gold Surfaces,"** in Secondary Ion Mass Spectrometry, SIMS X, John Wiley and Sons, 1995 (in press).

25. *Particle Imaging with the Scanning Electron Microscope for Particles-in-Oil SRM*

J. Verkouteren, R.A. Fletcher, D.S. Bright, E.S. Windsor, J.A. Small, and E.B. Steel

Objective: To characterize particle sizes by SEM imaging to produce a new SRM for particles in oil.

Problem: Oils containing known particle numbers and sizes are required to calibrate optical particle counters. The material chosen as an SRM for this purpose is an oil containing a natural road dust (ISO Medium Dust). The particles, which range in size from 0.5 μm to 30 μm, must be quantitatively separated from the oil by filtration and accurately sized and counted. Thousands of particles per size class must be counted to certify the SRM.

Approach: The SEM was chosen for image collection to cover the wide range of particle sizes and to allow chemical analysis of selected particles for identification purposes. An automated image collection and analysis system was designed to sample the thousands of particles required for certification. The image collection parameters necessary to obtain images amenable to computer analysis were investigated.

Results and future plans: We developed a working procedure for collecting the images, overcoming several technical challenges and difficulties. The filters upon which the particles are deposited are the most appropriate for quantitative separation, but are notorious for charging from the electron beam, which can profoundly affect images and quantification. We found that a thin coating of Au using a plasma coater partially alleviates the charging problem, and does not limit the contrast of the smaller particles or physically damage the filter. We found the backscattered electron signal to be the most useful for image collection because it is less sensitive to charging effects. The contrast in the backscattered electron images is largely influenced by topographic variations, and is not a simple function of differences in average atomic number as for flat samples. The contrast between the particles and the filter background is sufficient to allow the particles to be discriminated by grey-level thresholding of the images.

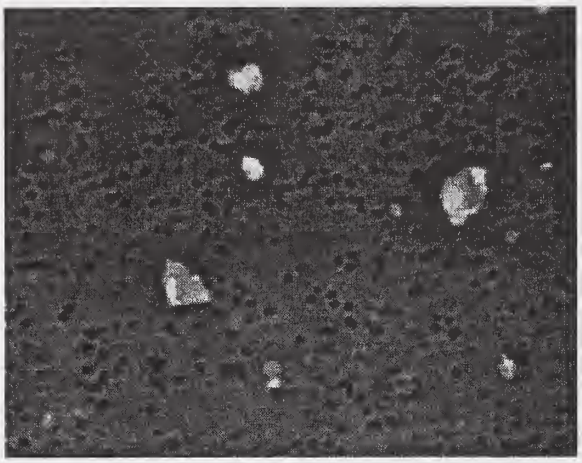


Figure 1. SEM backscatter image of particles on 0.2 μm pore size filter.

We also developed a standard procedure for collecting images randomly over the surface of a given filter at a series of magnifications to obtain representative samplings. A computer program developed at NIST determines the perimeter of the filter based on the input of 4 fiducial points, randomly selects as many fields as requested within the determined filter area, and then controls the instrument to move to the selected locations and collect the images. The human interaction required includes the initial setup of the SEM for image collection, and the adjustment of the stage height for each selected image to bring the sample to optical focus. The stage height for each image is recorded during the setup procedure and is faithfully reproduced during the automated image collection.

In FY96 we plan to complete the image collection for the particles-in-oil standard, using the procedures developed this year, analyze the filters to determine homogeneity and use QA to assure accuracy of the measurements.

V. Thermophysics Division (838)

Richard F. Kayser, Chief

A. Division Overview

Mission:
The Thermophysics Division is the Nation's reference laboratory for measurements, standards, data, and models related to the thermophysical properties of fluids and fluid mixtures; process separations; pressure, vacuum, partial pressure, and low flow rate; and cryogenic technologies. The Division develops and maintains state-of-the-art experimental, theoretical, and modeling capabilities and provides technical research and services to enhance the productivity and competitiveness of U.S. industry and to assist U.S. industry, other government agencies, and academia in solving problems of national importance.

Programs:
The **thermophysical properties of fluids and fluid mixtures** are essential to the competitiveness of the chemical and related industries to ensure innovation in process design and control, improvements in equipment performance, and equity in trade. The Division's research comprises experimental, theoretical, and computer simulation studies of the equilibrium, transport, and interfacial properties of pure fluids and fluid mixtures. The experimental research entails the acquisition of highly accurate thermophysical properties data and the development of new, state-of-the-art measurement techniques. The fluids studied are representative of broad classes encountered in many industries; they include common inorganic chemicals, hydrocarbons and hydrocarbon mixtures, aqueous solutions, and new working fluids, such as alternative refrigerants. In synergism with the experimental programs, the Division critically evaluates and correlates thermophysical properties data and conducts research on fundamental theoretical models, new concepts and phenomena, and predictive algorithms. The results of these efforts appear as conventional correlations and tables and as predictive computer codes.

Separation processes play a central role in the chemical and related industries in areas ranging from the isolation and purification of products to the removal of impurities and contaminants from chemical process and waste streams. Separations often account for more than 50% of the capital and operating costs of a chemical process. The Division's program in this area involves basic and applied research on commercial-scale separation processes and technologies, including distillation, extraction, membrane separations, and adsorption; the program also includes research on process analytical chemistry aimed at improving process control. The goals of the research are to develop state-of-the-art measurement techniques and models to characterize transport processes and other phenomena central to process separations and to provide critically-evaluated physico-chemical data and models needed to develop more robust and species-specific separation processes.

Accurate **pressure, vacuum, and low-flow-rate measurements and standards** are vital to assure process and product quality in the chemical, semiconductor, energy and power, automotive, aerospace, and defense-related industries. The goals of the Division's research are to develop new and more accurate measurement methods and concepts and to disseminate the U.S. national measurement standards for pressure, vacuum, and low flow rate. The pursuit of these goals requires in-depth investigations of pressure, vacuum, and low-flow-rate instrumentation, including piston gages, ultrasonic interferometer manometers, pressure transducers, ionization gages, spinning rotor gages, partial pressure analyzers, and low-range flow meters. The Division provides calibration services for pressure and vacuum (from 10^{-7} to 10^{-9} Pa) and for low flow rate (from 10^{-14} to 10^{-4} mol/s) and offers precision measurement workshops in these areas.

Cryogenic technologies underpin a wide variety of technically important areas, including the cooling of

electronics for high-speed computing and communications, the production of ultra-clean environments for semiconductor manufacturing processes, the liquefaction of natural gas from remote gas wells and for use as a clean fuel, the cooling of medical instruments, and the cooling of satellite-based infrared sensors for military and environmental applications. Research in this area concentrates primarily on the development of new and improved cryocooler processes, especially pulse-tube refrigerators, capable of operating at temperatures from 120 K to below 10 K. The program encompasses the development of improved measurement and modeling techniques needed to characterize cryocooler components and to improve their performance. Other areas of emphasis include research on cryogrinding and on methods of measuring cryogenic flows.

During the past year, the Division continued its comprehensive program on the **thermophysical properties of chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) alternatives**. CFCs and HCFCs are pervasive in modern society as the working fluids in small and large-scale air-conditioning and refrigeration equipment, but because of their link to the depletion of stratospheric ozone, industry must replace them with non-ozone-depleting alternatives in accordance with the revised Montreal Protocol and the 1990 Amendments to the Clean Air Act. The objectives of the Division's program are to acquire highly accurate thermophysical properties data for the most promising alternatives (both pure fluids and mixtures) and to develop models to predict their thermophysical properties. These data and models are essential to implement new fluids in existing equipment and to design and optimize new equipment. In addition to publications in the archival literature, the computer package, **REFPROP**, has become a principal vehicle for disseminating the Division's research on alternative refrigerants. REFPROP now calculates the equilibrium and transport properties of 41 pure refrigerants and mixtures with as many as five components, and it includes high-accuracy multiparameter equations of state for 14 of the most promising pure refrigerants. The NIST Standard Reference Data Program has distributed almost 500 copies of REFPROP, and the Air Conditioning and Refrigeration Institute and the Electric Power Research Institute have adopted REFPROP as the primary source of thermophysical properties data for their Alternative Refrigerants Evaluation Program. Future efforts in this area will concentrate on the identification and characterization of alternatives to the HCFCs and related fluids. The emphasis will be on mixtures, since there are no obvious pure fluids that could serve as substitutes for the fluids currently in use.

The research on alternative refrigerants is part of a broader effort to provide accurate and comprehensive thermophysical properties data and models for the properties of **advanced working fluids**. This information is essential to design and optimize the performance of power plants and refrigeration systems based on promising new technologies. Projects in this area are focusing on ammonia-water mixtures as alternatives to steam as the working fluid in power cycles, and on mixtures of noble gases as working fluids for large-scale thermoacoustic refrigerators. Recent developments indicate that ammonia-water mixtures may improve energy efficiencies significantly compared to steam in applications ranging from direct-fired power plants with high operating temperatures to geothermal power plants with relatively low operating temperatures.

The **properties of pure and mixed hydrocarbons**, such as natural gas and its components, continue to be topics of significant emphasis for the Division. The objectives of several projects are to provide the natural gas industry and the consumer with the validated property data and models needed for accurate custody-transfer transactions and for the design, control, and optimization of gas processes. Most recently, the American Society for Testing and Materials and the Compressed Gas Association have adopted standards for the properties of several key natural gas components based on Standard Reference Databases developed by the Division. In a related project, the Gas Processors Association has supported measurements within the Division of the densities of several natural gas liquid components and their mixtures. The purpose of this work is to improve the accuracy of the volume correction factors used in the custody transfer of natural gas liquids. Along slightly different lines, the Gas

Research Institute is supporting work aimed at standardizing the chemical analysis of the fraction of natural gas with components consisting of six or more carbon atoms. The goal is to assign more accurate heating values to natural gas mixtures.

The **development of new experimental apparatus** to determine the thermophysical properties of industrially important fluids and fluid mixtures is a vital component of the Division's overall program. Specific measurement capabilities completed during the past several years or under development at present include new apparatus for transport properties (tantalum-hot-wire thermal-conductivity apparatus, vibrating-wire viscometer, acoustic resonators for measuring the transport properties of gases), thermodynamic properties (dual-sinker densimeter, high-temperature vibrating-tube densimeter, total-enthalpy flow calorimeter), phase equilibria properties (recirculating phase equilibrium apparatus, azeotropic vapor-liquid-equilibrium apparatus, low- and high-pressure ebulliometers), and dielectric properties (concentric-cylinder dielectric-constant apparatus, re-entrant radio-frequency resonator). Many of these apparatus are of all-metal construction and easy to automate, and hence suitable for a wide variety of uses in both research and the chemical process industry.

The Thermophysics Division's **Fluid Properties Data Center** comprises another set of major activities. The Data Center compiles, evaluates, and correlates data on the thermodynamic and transport properties of industrially important fluids and fluid mixtures and develops new theories, models, and predictive algorithms. The Data Center also produces several well-known microcomputer databases for calculating thermophysical properties, including REFPROP, described above; all of these databases are available through the NIST Standard Reference Data Program. The Fluid Properties Data Center is also responsible for the Division's theoretical and modeling research on the properties of aqueous systems. For example, the Data Center and the Process Measurements Division are collaborating on a project on the **hydrothermal processing** of hazardous and toxic wastes. This technology exploits the fact that a wide variety of complex materials can be hydrolyzed and oxidized to mostly innocuous products under the relatively mild conditions of water near its critical point. A long-term goal is to develop comprehensive models for the properties and phase behavior of aqueous mixtures containing salts, air components, and organic and inorganic compounds.

Based on numerous industrial interactions, meetings, and workshops, the Division is pursuing several promising new directions in the area of thermophysical properties. In **Structure-Based Modeling**, the Division is working to develop and validate state-of-the-art models for predicting the thermophysical properties of a wide range of industrially important chemicals and chemical mixtures over extended operating ranges based on molecular structure alone. This program will address the long-term needs of chemical process simulators and involve close collaborations with organizations such as the Design Institute for Physical Properties Data (DIPPR®). The aim of the program on **Dilute Solutions** is to develop state-of-the-art measurement capabilities, databases, and models for estimating the thermophysical properties of dilute multicomponent mixtures over wide ranges of temperature, pressure, and composition, with and without chemical reactions. The results will have a major impact on the design and optimization of processes for removing dilute contaminants from process and effluent streams in the chemical and related industries. Work in the area of **Computational Thermophysics** will concentrate on the quantitative calculation of the physical and chemical properties of solutions using classical and quantum molecular dynamics and Monte Carlo simulation codes. Finally, the goals of the program on **Semiconductor Gases** are to develop and use novel acoustic techniques to measure the equilibrium and transport properties of the 50 or so gases critical to semiconductor manufacturing processes; these data are essential to develop and validate property estimation schemes, to validate computational chemistry calculations, and to characterize instrumentation widely used in the semiconductor industry. These same acoustic techniques are the linchpin of a new NIST program on **Improved Primary Thermometry Above 500 K**.

In the area of process separations, there has been renewed interest in the development of industrial processes based on **supercritical fluid extraction** (SFE). The best candidates for SFE are high-cost, low-volume chemicals that require the use of nontoxic solvents, e.g., natural products for human consumption. Although carbon dioxide is the supercritical fluid investigated most frequently in the past, its nonpolar properties limit its applicability. Because of this, the Division has begun to focus more heavily on the use of alternative refrigerants as supercritical fluid extractants. Many of these fluids are highly polar as well as nontoxic, which makes them superior solvents for many applications compared to carbon dioxide and mixtures of carbon dioxide and polar additives. In the area of **membrane separations**, research is concentrating on the use of polymeric membranes to separate gas mixtures. The goal is to elucidate the fundamental relationship between the microscopic physical and chemical properties of membranes and their separation characteristics. Much of the Division's remaining research on separations is focusing on **environmental separations**, which is appropriate given the emphasis within the chemical and related industries on waste minimization and pollution prevention. Recent work on membranes included an assessment of different approaches to removing contaminants from wastewater. Another area of significant interest is separations based on fluid-solid **adsorption**. An initial goal was to evaluate the state of the art of low-cost sorbents for separating a wide variety of metals from aqueous waste streams. Longer-term goals are to develop databases and models for predicting the adsorption characteristics of priority pollutants on low-cost sorbents and models for the dynamics of adsorption and sorbent regeneration processes.

Recent advances in the **measurement of pressure and vacuum** include the development of **new standards and calibration services** as well as significant **improvements in instrumentation**. In the range near and above atmospheric pressure, the Division is engaged in a collaboration with DH Instruments, Inc. to characterize the world's first 50-mm-diameter piston gages; these large-diameter gages have the potential to become primary standards in the important range near atmospheric pressure. Efforts are also well underway to provide new services for calibrating gas-operated piston gages up to 110 MPa and high-pressure, oil-operated gages and transducers up to at least 500 MPa. In the range near and below atmospheric pressure, the Division has reduced the uncertainties of its high-accuracy Ultrasonic Interferometer Manometers and has addressed a long-standing gap in NIST's primary vacuum standards where many important industrial processes operate, including sputtering and plasma processing of semiconductors. Finally, work on vacuum instrumentation has progressed beyond the characterization of performance to the development of improved instruments. For example, a new PC-based spinning rotor gage controller developed in-house will broaden the use of that technology significantly for a variety of applications, including process control.

Based on information collected through industrial interactions, technology roadmapping activities, meetings, and workshops, the Division has initiated several new thrusts in the area of **semiconductor processing**. One major new thrust is to develop ***in situ* partial pressure measurement methods and standards** to calibrate vacuum instrumentation for use with process gases. This effort will expand vacuum metrology beyond the traditional inert gases to include low-level contaminants in higher-pressure background gases. Such contaminants play a critical role in determining the quality of vacuum-processed components and represent a major challenge from the point of view of real-time process monitoring and control. Research projects in this area include the development of **quantitative optical reference standards** based on non-intrusive, species-specific techniques such as resonance enhanced multiphoton ionization and ring-down cavity absorption, and the development of **improved instrumentation** for measuring process partial pressures. Inasmuch as water is one of the most common contaminants in processes that operate at reduced pressures, the Division is focusing its near-term efforts on the measurement of low-density water vapor. The absolute and partial pressures of interest range from 10^{-8} to 10^{-1} Pa. With regard to improved instrumentation, the Division is extending its original studies of Residual Gas Analyzers (RGAs) to elucidate the fundamental

causes of their metrological deficiencies and to identify possible solutions. However, it is clear that even with refined RGAs, it will be necessary to calibrate instruments regularly in the processing chamber; thus, efforts are underway to develop *in situ* calibration systems and techniques based on flow generators.

A second major thrust in the semiconductor area is the development and dissemination of **new standards for low flow rates** for a variety of gases. The goal is to address industry's needs for reliable and accurate flow measurements in the important range from 0.1 to 100 standard cm^3/min (10^{-7} to 10^{-4} mol/s). During the past year, the Divison has constructed two new constant-volume primary flow standards based on the pressure rate-of-rise technique and has shown that they agree with existing constant-pressure primary flow standards to within 0.1%. A parallel effort has culminated in the development of a set of very robust transfer standards for low flows based on laminar-flow elements of novel design; these devices will enable NIST to intercompare its flow standards with flow standards elsewhere. Finally, the Division has completed its first critical evaluation of the operational characteristics of thermal mass flow meters, which are used throughout the semiconductor industry to deliver stable and known flows of gases to processing chambers. This evaluation focused on five commercially available thermal mass flow meters with full-scale ranges of 2 to 5 standard cm^3/min. This comprehensive study covered nitrogen, argon, helium, hydrogen, sulfur hexafluoride, and hexafluoroethane over a range of operating conditions, including variable temperature, meter orientation, and upstream pressure.

Until recently, the poor reliability, high cost, low efficiency, and in some cases, high vibration of **cryocoolers** have hampered the advancement of many technologies that require low temperatures. The objective of the Division's program in this area is to support the development of new technologies and processes, especially pulse-tube refrigerators, that do not have these limitations. Research during the past few years has resulted in the development of a thermoacoustically-driven orifice pulse-tube refrigerator, which was the world's first refrigerator to achieve cryogenic temperatures with *no moving parts*. In addition, the Division's research has improved the performance and efficiency of pulse-tube refrigerators by factors of 2 to 5 and has reduced the lowest temperature achieved from above 100 K to below 10 K. These pioneering advances have made the Division the focal point for cooperative research and development efforts with numerous organizations, including TRW, Hughes Aircraft, Lockheed Martin, Tektronix, GE, BEI, Cryenco, the Ballistic Missile Defense Organization, the U.S. Air Force, the U.S. Navy, and NASA. For example, NASA recently selected orifice pulse-tube refrigerators for use in the Atmospheric Infrared Spectrometer to be placed on board the Earth Observing Satellite.

Awards in FY95:

Several members of the Thermophysics Division received significant recognition during the past year. Dr. Charles R. Tilford received the Department of Commerce Gold Medal for his leadership and technical contributions in establishing NIST's world-class programs on vacuum and low-flow-rate measurements and standards. Dr. Ray Radebaugh received the Department of Commerce Silver Medal for outstanding contributions to the development and implementation of advanced low-temperature refrigeration systems. Dr. Marcia L. Huber received a NIST Measurement Service Award for developing OILTRAPP, a new computer package for predicting the transport properties of petroleum fractions, and Mr. R. Gregory Driver received a NIST Measurement Service Award for outstanding contributions to the development and characterization of next-generation primary pressure standards.

Organizational Structure:

The Thermophysics Division consists of seven groups: Process Separations, Fluid Science, Pressure, Vacuum, Experimental Properties of Fluids, Theory and Modeling of Fluids, and Cryogenic Technologies. Of these, Fluid Science, Pressure, and Vacuum are located in Gaithersburg, MD; the others are located in Boulder, CO. The following Technical Reports describe the activities and major accomplishments of these groups in more detail.

B. Selected Technical Reports

1. *Thermophysical Properties of Alternative Refrigerants*

M.O. McLinden, D.R. Defibaugh, R.A. Perkins, K.A. Gillis, C.D. Holcomb, M.R. Moldover, M.L. Huber, A.R. Laesecke, J.W. Magee, D.G. Friend, S.L. Outcalt, J.W. Schmidt, W.M. Haynes, L.A. Weber, N. Kagawa (National Defense Academy, Yokosuka, Japan), E.W. Lemmon (Univ. of Idaho), R. Tillner-Roth (Univ. of Hannover, Germany), S.A. Klein (Univ. of Wisconsin), and L. Cuscó (Imperial College, London, UK)

Objective: Provide industry with high-accuracy property data and models for alternative refrigerants and refrigerant mixtures.

Problem: The CFC and HCFC refrigerants must be replaced with fluids which do not deplete stratospheric ozone. A number of very promising alternatives, primarily hydrofluorocarbons (HFCs) and HFC mixtures, are currently under development. Refrigerant mixtures are becoming increasingly important as alternative refrigerants, particularly as replacements for HCFC-22. To evaluate the performance (energy efficiency, capacity, etc.) of any fluid in a thermodynamic cycle or to design equipment using a new fluid, a knowledge of the thermophysical properties is required.

Approach: Our work on alternative refrigerants represents a comprehensive approach to a major problem and has been supported by multiple government agencies and industry groups. The Division's work in this area includes experimental measurements at several levels of detail (ranging from screening measurements to standard reference data) and the compilation and evaluation of literature data. These data provide the input information for developing the models which form the basis of Standard Reference Database 23: Thermophysical Properties of Refrigerants and Refrigerant Mixtures (REFPROP). Also included are technology transfer activities and participation in international collaborations.

Results and Future Plans: During the past year comprehensive measurements including PVT, heat capacity, and vapor-liquid equilibrium (VLE) have been completed for the R32/125, R125/143a, and R134a/125 mixtures. More limited measurements (VLE data only) have been completed or are in progress for an additional six binary systems and one ternary system. The determination of the critical line is included for five of these systems. These data are being used in the mixture model comparisons of International Energy Agency (IEA) Annex 18, described below.

Speed of sound measurements are used to derive thermodynamic properties of the vapor phase, including the second and third virial coefficients, and the ideal gas heat capacity. This technique has been applied to seven fluids during the past year, including three fluorinated propanes - compounds which are potential replacements in a variety of applications, including large-building air-conditioning systems presently using CFC-11 or HCFC-123.

New measurements, together with literature data, were used to fit new or updated high-accuracy, standard-reference-quality MBWR equations of state for R152a, R143a, and R236fa. These equations were developed using a multivariable fitting technique that allows a simultaneous fit of all of the experimental data, including "higher order" data such as heat capacity and speed of sound; they are valid over very wide ranges of temperature, pressure, and density.

The measurement and correlation of transport properties (thermal conductivity and viscosity) are complementary to the study of the thermodynamic properties. During the past year, comprehensive measurements of the thermal conductivity and viscosity of R236fa and the thermal conductivity of R142b and R600 were completed. Liquid-phase viscosity measurements for R236ea and R236fa were completed using a capillary technique, and vapor-phase viscosities of R134a, R143a, R152a, R236ea, and R236fa were made using a torsional crystal viscometer. Calculational models for the transport properties of refrigerants and their

mixtures are being developed using an extended-corresponding-states formalism.

Publications:

Gillis, K.A., **"Thermodynamic Properties of Seven Gaseous Halogenated Hydrocarbons from Speed of Sound Measurements: 1-chloro-1,2,2,2-tetrafluoroethane, pentafluoroethane, 1,1,1-trifluoroethane, 1,1-difluoroethane, 1,1,1,2,3,3-hexafluoropropane, 1,1,1,3,3,3-hexafluoropropane, and 1,1,2,2,3-pentafluoropropane,"** Int. J. Thermophysics (in press).

Outcalt, S.L. and McLinden, M.O., **"A Modified Benedict-Webb-Rubin Equation of State for the Thermodynamic Properties of R152a (1,1-difluoroethane),"** J. Phys. Chem. Ref. Data (in press).

2. *Database for the Chromatographic Analysis of Alternative Refrigerants*

***T.J. Bruno**, K.H. Wertz (Univ. of Colorado), and M. Caciari (Ft. Lupton High School, CO)*

Objective: The goal of this research is to provide an efficient and reliable method of identifying and quantifying alternative refrigerants, their synthetic precursors, and potential decomposition products. This goal will be achieved with an interactive database of standard chromatographic retention parameters that can be incorporated into the control software of laboratory and process gas chromatographs.

Problem: The identification and analysis of alternative refrigerants (and their synthetic precursors and decomposition products) is a necessary ingredient of thermophysical property measurement; refrigerant synthesis, formulation and manufacture; and the operation of machinery and refrigeration plants. A fast, economical, and reliable method of analysis is necessary for both laboratory applications and for in-line and at-line process analytical determinations. While some spectroscopic approaches offer specific identifications and analyses, chromatography provides the only means to a general scheme. It is also one of the most economical and well understood methods available.

Approach: We have approached the standardization and automation of the identification and analysis of these materials by measuring standard chromatographic retention parameters as a function of column temperature for the most valuable stationary phases that can be applied to light halocarbons. The standard retention parameters include relative retentions, net retention volumes, and Kovats retention indices. The measurements are performed on a specially modified gas chromatograph that provides highly accurate retention measurements. The column temperature dependence of these parameters are then modeled with an appropriate mathematical expression to allow prediction at all temperatures. These models are part of an interactive database that allows off-line identification and optimization of

more complex analyses. Ultimately, the database will be incorporated into the control software of a process gas chromatograph.

Results and Future Plans: The measurement of all standard retention parameters at four column temperatures (ranging from -20 to 160°C) have been completed for the first stationary phase, a 5% coating of hexafluoropropyl epoxide on graphitized carbon black. In addition, relative detector response factors have been measured for the thermal conductivity detector. These results are being assembled into an interactive database.
During the next year, we will make standard retention parameter measurements (again at four column temperatures over an appropriate range) on a 5% phenyl polydimethyl siloxane capillary column phase. These data will then be added to the database.

Publications:

Bruno, T.J. and Caciari, M., "**Retention of Halocarbons on a Hexafluoropropyl Epoxide Modified Graphitized Carbon Black: Part I - Methane Based Fluids,**" J. Chromatography A 672, 149-158 (1994).

Bruno, T.J. and Caciari, M., "**Retention of Halocarbons on a Hexafluoropropyl Epoxide Modified Graphitized Carbon Black: Part III - Ethene Based Fluids,**" J. Chromatography A 686, 245 (1994).

Bruno, T.J., "**Permeation Tube Approach to Long Term Retention Index Standards,**" J. Chromatography A 704, 157-162 (1995).

Bruno, T.J. and Wertz, K.H., "**Retention of Halocarbons on a Hexafluoropropyl Epoxide Modified Graphitized Carbon Black, Part VI: Eleven Fluoroethers and Two Iodofluoroalkanes,**" J. Chromatography A (in press).

Bruno, T.J., Wertz, K. H., and Caciari, M., "**Kovats Retention Indices of Halocarbons on a Hexafluoropropyl Epoxide Modified Graphitized Carbon Black,**" Anal. Chem. (in press).

3. International Activities on CFC and HCFC Alternatives

M.O. McLinden, R.A. Perkins, and M.L.V. Ramires (Univ. of Lisbon, Portugal)

Objective: Promote international cooperation in the study of the thermophysical properties of alternative refrigerants.

Problem: Many laboratories around the world are engaged in the study of thermophysical properties of the alternative refrigerants. International coordination of these activities is needed to avoid duplication of effort and to speed the development of refrigeration equipment using the new working fluids. Numerous data sets and property models are now appearing in the literature and are sometimes in disagreement; the proliferation of property values peculiar to a nation or even an individual company poses problems in trade. Evaluation of data and models is needed to arrive at internationally accepted property formulations.

Approach: Division personnel are active in numerous international organizations and committees including Annex 18 of the International Energy Agency (IEA), the Thermodynamics Subcommittee on Transport Properties of the International Union of Pure and Applied Chemistry (IUPAC), and the Refrigeration Technical Options Committee of the United Nations Environment Programme (UNEP).

Results and Future Plans: The Thermophysics Division initiated and serves as "operating agent" (coordinator) for IEA Annex 18 - Thermophysical Properties of the Environmentally Acceptable Refrigerants. The objectives of this project are (1) to provide a forum for the exchange of information and data and for the coordination of activities on the thermophysical properties of environmentally acceptable refrigerants, and (2) to determine the thermophysical properties of these fluids (including experimental measurements, and the evaluation and correlation of data) leading to the publication of comprehensive, internationally accepted property bulletins.

During FY95, NIST coordinated a comparison and evaluation of refrigerant mixture models including establishing a database of mixture property data accessible to the Annex participants. The evaluation process focused on two reference mixtures (R32/125 and R32/134a); results from a preliminary comparison were presented at the August 1995 meeting of the Annex. These comparisons were used to plan additional experimental work which will feed into a second round of comparisons scheduled for September 1996. In another major task, the evaluation of equations of state for the properties of pure R32 and pure R125 has begun. The NIST model for the thermodynamic properties of R123, accepted last year as the international standard, was published during FY95 as a "scientific paper" and as a "properties bulletin" aimed at the practicing engineer.

The Division is an active participant in IUPAC activities on the transport properties of the alternative refrigerants. The highly polar HFC refrigerants present special difficulties for many of the standard measuring techniques, and NIST has organized an international round-robin test series on a standard sample of R134a. Preliminary comparisons have been published. NIST will prepare new standard reference correlations for the viscosity and thermal conductivity of R134a in the coming year as part of the final report for this project.

The Division has also participated in the third technical reassessment associated with the Montreal Protocol on Substances that Deplete the Ozone Layer, the international treaty which regulates the production of CFCs and HCFCs. M.O. McLinden serves on the refrigeration and air-conditioning panel and was lead author for the "Refrigerant Data" section. This process provides input for the periodic renegotiation of the phase-out timetable and other provisions of the Protocol. A preliminary meeting for a possible fourth technical reassessment was held in October 1995.

Publications:

Assael, M.J., Nagasaka, Y., Nieto de Castro, C.A., Perkins, R.A., Stom, K., Vogel, E., and Wakeham, W.A., "**Status of the Round-Robin on the Transport Properties of R134a**," Int. J. Thermophysics 16, 63-78 (1995).

Younglove, B.A. and McLinden, M.O., "**R123 Thermodynamic and Physical Properties, Section 1 - Equation of State Formulation of the Thermodynamic Properties**," International Institute of Refrigeration Bulletin, Paris, France (in press).

Younglove, B.A. and McLinden, M.O., "**An International Standard Equation of State for the Thermodynamic Properties of Refrigerant 123 (2,2-Dichloro-1,1,1-Trifluoroethane)**," J. Phys. Chem. Ref. Data 23, 731-779 (1994).

4. *Ammonia-Water Mixtures for Use in Power Cycles*

D.G. Friend, J.C. Rainwater, M.L. Huber, C.D. Holcomb, J.W. Magee, R.A. Perkins, A.L. Olson (Univ. of Colorado), A. Nowarski (Univ. of Cracow, Poland), R. Tillner-Roth (Univ. of Hannover, Germany), and T. Lüddecke (Univ. of Hannover, Germany)

Objective: Establish standard reference thermophysical property surfaces for mixtures of ammonia and water over a broad range of temperature, pressure, and composition.

Problem: Improvements in the efficiency of power generation plants are often made in the areas of heat exchangers, combustion engineering, turbine design, more extreme operating conditions, and development of combined cycle operations. Current plants operate with a standard Rankine cycle using steam, and recent improvements have been somewhat marginal. Drastically redesigned systems have been proposed, however, which use the binary ammonia-water system as a working fluid, and dramatic increases in efficiency have been predicted. Pilot scale plants have been operated using this new technology, and major industrial players have obtained license agreements to implement this approach. In addition to certain engineering and other practical concerns, problems in the optimization of these new cycles and in the development of performance warranty protocols, have not been resolved because of uncertainty in the properties of the working fluid. This binary system is also the working fluid in some refrigeration applications, where again, reliable standard property information will assist in the optimization of designs.

Approach: The first phase of the project included an extensive bibliographic study to evaluate the existing relevant property data and models. Experimental studies of key properties for the system will be carried out. Existing scaling theory approaches can be used for a study in the high pressure region, and phase boundary calculations can be done with cubic equations of state; however, an accurate surface requires a more sophisticated model. Several versions of an extended-corresponding-states (ECS) algorithm are being modified for this fluid, and a two-fluid Helmholtz energy model is also being developed.

Results and Future Plans: During FY95, data collection and organization have continued, including acquisition of the extensive recent, yet unpublished, data from the University of Hannover. More than 10,000 experimental points have been converted to standardized units and formats; deficiencies and inconsistencies in some regions of the phase diagram have been noted. The scaling theory approach for the high pressure VLE region has been used to generate densities for the general thermodynamic surface, and this procedure is being iterated to establish an accurate self-consistent formulation. The ECS model is being modified to improve the low density region, and faster and more robust calculational methods for establishing the state-dependent shape factors are being developed. Nonlinear optimization procedures for the binary interaction parameters have been implemented, and additional degrees of freedom have been introduced in these factors to allow extension of the model. A preliminary computer program for calculations in a limited region of the phase diagram was sent to the Department of Energy and to several industrial partners. The two-fluid Helmholtz energy model is being pursued as an alternative approach. Although this may not have the predictive capabilities of the ECS algorithm, it may be appropriate for binary systems with extensive experimental data.

The safety issues related to the ammonia-water system have been evaluated, and experimental protocols have been established. Test experiments with pure water have been performed. Diaphragm cells have been constructed for preparation of the liquid mixtures; this eliminates problems associated with demixing. Selected measurements for the binary system, concentrating on the ammonia-rich end, will be completed in the coming year. The new VLE, density, heat capacity and thermal conductivity data will be used to optimize the models.

Publications:

Friend, D.G., Olson, A.L., and Nowarski, A. "**Standard Thermophysical Properties of the Ammonia-Water Binary Fluid,**" in **Physical Chemistry of Aqueous Systems**, Proc. 12th Int. Conf. on the Properties of Water and Steam: Meeting the Needs of Industry, Begell House, New York, 1995, H.J. White, Jr., J.V. Sengers, D.B. Neumann, and J.C. Bellows (eds.), pp. 854-861.

5. *Properties of Helium-Xenon Mixtures for Thermoacoustic Refrigerators*

J.J. Hurly, K.A. Gillis, and M.R. Moldover

Objective: Provide thermophysical property data for optimizing the design of thermoacoustic refrigerators.

Problem: Thermoacoustic refrigerators exploit a nonlinear interaction between very-large-amplitude sound waves and a suitably designed heat exchanger to pump heat. Theoretically, the optimum working fluids for such refrigerators are specific mixtures of helium and xenon. These mixtures are advantageous because they have low Prandtl numbers and acceptably large values of C_p/C_v. Accurate data for the relevant mixtures are not available.

Approach: NIST-acquired equation-of-state data and speed-of-sound data will be combined to determine the thermodynamic properties. Acoustic resonators will be used to determine the viscosity and the Prandtl (Pr) number. [$Pr \equiv$ (viscosity × heat capacity)/(thermal conductivity)].

Results and Future Plans: During FY95, the equations of state of helium, xenon, and three helium-xenon mixtures were measured using the Division's semi-automated Burnett apparatus. The manufacturer had prepared mixtures with nominal mole fractions of 0.25, 0.50, and 0.75 xenon. However, these compositions were inaccurate; we determined accurate values of the compositions from low-pressure speed-of-sound measurements. The equation of state data span the temperature range 273 - 373 K and the pressure range 0.5 - 5 MPa and lead to densities with an uncertainty of 0.01 %.

During FY96, the speed of sound will be measured in helium, xenon, and the same three mixtures. The data will span the temperature range 210 - 400 K and the pressure range 0.05 - 1.5 MPa and have an uncertainty of 0.01 %. The speed-of-sound data and equation-of-state data will be analyzed simultaneously using a virial equation of state. The results for pure helium will be checked by

comparison to *ab initio* calculations. During FY96, NIST shall also measure the transport properties of the pure gases and of the mixtures using the Greenspan acoustic viscometer and the acoustic Prandtl-number meter described below. All of the data will be used to validate and update the NIST-developed computer program NOBLEG.

6. *Acoustic Resonators for Measuring the Transport Properties of Gases*

***K.A. Gillis**, J.B. Mehl (Univ. of Delaware), and M.R. Moldover*

Objectives: Develop robust instruments for measuring the viscosity and Prandtl number of gases, including the reactive and toxic gases used in semiconductor processing.

Problem: Accurate data for transport properties of gases are needed to rationalize the metering of gases and to optimize the design of heat exchangers using gases. Instruments for measuring the transport properties of gases are fragile and expensive to use. Acoustic instruments have the potential of being robust and accurate under a wide range of conditions; however, sophisticated algorithms are required to interpret the data. NIST will optimize the design of these instruments and develop algorithms for interpreting the data obtained with them.

Approach: For measuring the viscosity, we have developed the Greenspan acoustic viscometer. This compact device is comprised of two cavities connected by a long narrow duct. A typical cavity has a volume of 30 cm^3; a typical duct is 6 cm long and has a diameter of 5 mm. The gas oscillates between the cavities by passing through the duct, which is where most of the viscous dissipation occurs. This viscometer does not require calibration; the viscosity can be deduced from its frequency response and dimensional measurements. Within the instrument, the test gas is in contact only with metal parts, typically of stainless steel and gold.

The Prandtl (Pr) number is the key parameter governing heat transfer from a solid to a flowing gas. [$Pr \equiv$ (viscosity $\times$ heat capacity)/(thermal conductivity)] . For measuring the Prandtl number, NIST has developed a cylindrical resonator with an insert comprised of an array of plates parallel to the cylinder axis. Typically, the array is located near the middle of the resonator and is 1/10 of the length of the resonator. The motion of the test gas in the vicinity of the array causes large losses, either from

the viscosity of the gas or its thermal conductivity, depending upon the resonance mode chosen. The Prandtl number is deduced from measurements of the frequency response of the resonator in the vicinity of several modes. Remarkably, the analysis does not require accurate, difficult-to-make dimensional measurements such as the area of the array.

Results and Future Plans: During FY95, the theory of the Greenspan viscometer was completed and two prototype instruments were constructed and tested with helium, argon, and propane. For each of these instruments, the results for the viscosities of the three gases were consistent within ±0.5% at pressures spanning the range 25 kPa - 1000 kPa. There remain discrepancies between the data and the theory for the instruments; however, the results are sufficiently encouraging that a manuscript has been submitted describing the results.

During FY96, additional development of the Greenspan viscometer will occur. Prototype instruments for measuring the Prandtl number will be fabricated and tested with several gases. The theory of this instrument will be refined and tested. The technical challenges of making robust electro-acoustic transducers for acoustic measurements of transport properties in reactive gases are similar to the challenges of making transducers for primary acoustic thermometry at high temperatures. We anticipate that the solutions to both problems will have common elements.

7. *Apparatus for State-of-the-Art Thermophysical Property Measurements*

***R.A. Perkins**, C.D. Holcomb, J.W. Magee, S.L. Outcalt, L.A.Watts, J. Blanco (Univ. of Colorado), L. Cuscó (Imperial College, London, UK), and T. Lüddecke (Univ. of Hannover, Germany)*

Objective: Develop new experimental measurement capabilities for the thermophysical properties of fluids and fluid mixtures to enable the U.S. to address critical problems related to energy.

Problem: Thermophysical-properties data are vital for process modeling and optimization and equipment design in a wide range of applications, including process simulation in the energy and chemical process industries and equipment simulation and design in the air-conditioning and refrigeration industry. Accurate property data and models based on these data are the key to generating results that can be used with confidence. These data are required for an ever-widening variety of fluids and fluid mixtures over wide ranges of temperature and pressure.

Approach: The development of experimental measurement capabilities for the thermophysical properties of energy-related fluids has been supported by the Department of Energy (DoE) for many years. State-of-the-art measurements carried out on apparatus developed under DoE sponsorship have been the cornerstone of our programs on the alternative refrigerants and natural gas and petroleum systems. These measurements also provide the data which are needed to develop the models which underlie our Standard Reference Databases.

Results and Future Plans: An apparatus to measure vapor-liquid equilibria (VLE), saturated liquid and vapor densities, and interfacial tension has been developed, calibrated, and performance tested over the last two years. This apparatus covers a wider temperature range (220 to 425 K) and has much improved temperature control compared to our previous apparatus. This apparatus has recently

been completed and is now used for measurements on refrigerant mixtures.

Development has been completed on a vibrating wire viscometer for measurements from 300 to 500 K with pressures to 70 MPa. This instrument can be used in both transient and steady-state modes on a wide range of fluids, including polar and electrically-conducting materials. A cryostat is currently under construction to extend the temperature range down to 80 K. A second vibrating wire viscometer is being designed for use on ammonia/water mixtures at temperatures to 700 K.

A total-enthalpy flow calorimeter is nearing completion. It will measure the enthalpy change, at constant pressure, of a fluid over a temperature interval within the limits of 200 to 500 K. It will, thus, allow the measurement of isobaric (constant pressure) heat capacity and the enthalpy of vaporization. The accuracy of the instrument is expected to be ±0.1%, which will be verified in the coming year with measurements on refrigerants.

Apparatus to be developed during the next three years include a small-volume, dual-cell, dew-bubble-point apparatus; a heat-of-vaporization calorimeter/effusion cell for the determination of vapor pressures below the normal boiling point; an apparatus for solubility measurements using magnetic levitation; a phase-equilibria apparatus for measurements on azeotropic aqueous/organic/ salt mixtures; and a light scattering cell for the determination of thermal diffusivity and critical point parameters.

8. *Properties of Natural Gas and Petroleum Systems*

J.W. Magee, C.D. Holcomb, W.M. Haynes, M.L. Huber, J.C. Rainwater, D.G. Friend, L.J. Van Poolen (Calvin College), J.F. Ely (Colorado School of Mines), M.E. Baltatu (Fluor Daniel, Inc.), and R.A. Chong (Fluor Daniel, Inc.)

Objective: Provide the thermophysical properties of natural-gas mixtures needed to develop and test predictive models, models for calculation of the transport properties of heavy petroleum fractions, and new theoretical approaches to describe the phase equilibrium behavior of hydrocarbon systems.

Problem: Validated thermophysical property data are essential to provide the natural gas and associated industries and the rate payer with the information needed for flow metering calculations associated with the sale (custody transfer) of natural gas or natural-gas liquids, for energy optimization in natural gas and petroleum industry operations, and also, for the design and control of processes in these industries. Additionally, models are needed to improve the ability to calculate properties of heavy petroleum fractions from the key parameters routinely determined in operating conditions, and to expand our understanding and representation for hydrocarbon systems for the broad range of conditions associated with industrial processes.

Approach: The Thermophysics Division has been engaged in a comprehensive experimental and theoretical research program for two decades to provide validated property data for natural-gas pure components and mixtures. This work has been supported primarily by the Gas Research Institute (GRI). In a current project sponsored by the Gas Processors Association (GPA), density measurements have been carried out on natural-gas-liquid components and mixtures. The purpose of this work is to improve the accuracy of ASTM (American Society for Testing and Materials) and API (American Petroleum Institute) standards for volume correction factors involved in custody-transfer calculations for natural-gas liquids (NGLs). The experimental work has been performed at NIST, while much of the modeling for NGLs has been done jointly with researchers at the Colorado

School of Mines. An extended-corresponding-states (ECS) approach, which imposes a mathematical transformation from a system of interest, including mixtures, to well studied thermophysical property surfaces for a reference fluid, has been well established for hydrocarbon systems. This algorithm can also be extended to poorly characterized heavy petroleum fractions. In the high pressure region, results from renormalization group approaches to the critical state can be developed for specific natural gas and petrochemical applications.

Results and Future Plans: During the past year, single-phase p,ρ,T measurements have been carried out on binary mixtures of ethane and propane and on a mixture of propane and normal butane. These measurements were made on an isochoric PVT apparatus at temperatures from 200 to 400 K at pressures to 35 MPa. With a vapor-liquid equilibrium apparatus, coexisting density and vapor-liquid equilibria data have been obtained for binary mixtures of ethane/propane, propane/normal butane, and normal butane/normal pentane over the complete composition range at temperatures from 240 to 420 K. Saturated liquid and vapor density measurements have been carried out on pure propane, normal butane, normal pentane, isopentane, and isohexane over a similar range of temperature.

During the past year, we also developed a predictive model for the temperature correction factor C_{TL} used in calculating volume correction factors for natural gas liquids from the relative density ρ_R and temperature. This model was tested with the new experimental measurements carried out in the first phase of this project. This project has reduced the uncertainty of the properties involved in the custody transfer of natural-gas liquids from 1.0 to 0.5%; a 0.5% uncertainty corresponds to more than $3 million on a monthly basis in the domestic market.

In FY96, a NIST Monograph will be prepared which presents detailed comparisons of natural-gas mixture density measurements with two internationally accepted predictive models (AGA-8 and GERG) for the density behavior of natural-gas mixtures. The experimental data used in these comparisons has arisen from an international round-robin series of density measurements aimed at providing the natural-gas industry with PVT standard reference data. This project, which has been sponsored and managed by GRI, is a cooperative effort between U.S. and European interests in the natural-gas industry.

The key parameters in defining heavy petroleum fractions include a standard specific gravity and a mean boiling point measurement. These two numbers can be used to understand the properties of mixtures containing literally hundreds of distinct species, by calculating effective values of critical point parameters, molar masses, acentric factors, etc., which can be used in the ECS approach to predict full thermodynamic and transport property surfaces. Work was done during this year on implementing and testing this approach for the thermal conductivity of such systems, and the continued development has resulted in a computer program (OILTRAPP) to predict properties directly from the key input.

Publications:

Ely, J.F., Haynes, W.M., Holcomb, C.D., and Magee, J.W., "**New Data and Correlations for the Custody Transfer of Natural Gas Liquids**," in Proc.74th Gas Processors Association Annual Convention, San Antonio, TX, 35-53 (1995).

Baltatu, M.E., Chong, R.A., and Huber, M.L., "**Viscosity of Defined and Undefined Hydrocarbon Liquids Using an Extended-Corresponding-States Model**," Int. J. Thermophysics 17, 213-221 (1995).

9. *Properties of Fluid Air at High Temperatures and Pressures*

D.G. Friend, E.W. Lemmon (Univ. of Idaho), M. Panasiti (Univ. of Idaho), and R.T. Jacobsen (Univ. of Idaho)

Objective: Establish reliable estimates for the thermodynamic and transport properties of fluid air including the extended range of temperatures and pressures up to 2000 K and 2000 MPa where data are not available.

Problem: Current wind tunnel technology is essentially limited to flow regimes with Mach numbers smaller than about Mach 10; however, an alternative which is being designed at Princeton University relies on a radiatively driven fluid stream and should achieve long-time flows at Mach 16. The design simulations and the final engineering parameters for such a hypersonic wind tunnel require air properties at extreme temperatures and pressures that have not been explored in conventional thermophysical property experiments.

Approach: We have previously studied the thermophysical properties of air, considered as a three-component mixture of nitrogen, oxygen, and argon, for temperatures from the solidification line to 870 K and for pressures to 70 MPa in conjunction with work on the National AeroSpace Plane project. In that study, we developed a thermodynamic formulation for the mixture based on a Helmholtz energy model, and we used an extended-corresponding-states approach for the transport properties. In this work, we will extend the previous study and will establish reliability of the correlation from the behavior of ideal curves, available high pressure data, conformality with other thermodynamic surfaces, and estimates of the effects of chemical decomposition.

Results and Future Plans: We have completed our literature search for relevant data in the region of interest. The existing surface for air has been optimized by including these data and by using a scaling argument based on data for nitrogen that are considerably more extensive. The behavior of the equation in the extrapolation region has been examined and validated. A computer program to implement this preliminary result has been developed and sent to the sponsors. We have examined the problems due to decomposition, and have found that the NO concentration does not significantly change our thermodynamic property surface. The project will be completed in 1996 with the development of transport property correlations based on an analogous procedure. Additional thermodynamic data, to be obtained from expansion nozzle experiments within the hypersonic wind tunnel, will be incorporated into the model as they are received.

Publications:

Jacobsen, R.T, Penoncello, S.G., Beyerlein, S.W., Lemmon, E.W., Friend, D.G., Ely, J.F., Rainwater, J.C., and Haynes, W.M., "**Thermophysical Properties of Air**," Supplement to NASP Technical Memorandum 1005, Version 5.0 (1995).

10. *Standard Reference Data for Thermophysical Properties of Fluids*

***D.G. Friend**, M.L. Huber, A.H. Harvey, M.O. McLinden, S.L. Outcalt, and S.A. Klein (Univ. of Wisconsin)*

Objective: The National Institute of Standards and Technology has a primary function to develop and disseminate standard reference data for the thermophysical properties of fluids and fluid mixtures of interest to the industrial and scientific communities.

Problem: The research and industrial communities have a need for very high accuracy thermophysical property data and models to optimize innovative design, to improve process efficiency, to mitigate environmental problems, to advance safety procedures, and to ensure equity in commodity trade.

Approach: Computerized databases provide the primary method of technology transfer of the high accuracy data and models developed at NIST. Additional mechanisms for transfer of this information include publication in archival journals, service on standards committees, and direct interaction with industrial users of this information.

Results and Future Plans: We currently support five computerized databases through the Standard Reference Data office of NIST: NIST4 (NIST Thermophysical Properties of Hydrocarbon Mixtures Database), NIST23 (NIST Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Database, also called REFPROP), NIST12 (NIST Thermophysical Properties of Pure Fluids Database), NIST14 (NIST Mixture Property Database), and NIST10 (NIST Thermophysical Properties of Water Database). During the past year we transmitted to SRD major upgrades of programs NIST12 and NIST23, and a minor upgrade of NIST4, and have been working on upgrades to the other databases and on development of new ones.

The new version of REFPROP, version 5.0, implements a high accuracy extended-corresponding-states model for refrigerant mixtures, adds new high accuracy MBWR formulations for the fluids R143a, R152a, and R236fa and introduces four new fluids (R116, propylene, R245ca and R236fa). Existing coefficients for the other refrigerants have also been updated using the latest experimental results. We also have significantly improved the operating speed of the database. The introduction of the extended corresponding states model for mixtures provides a major enhancement of the program. In FY 96, we will continue to add new fluids and improve our correlations for existing ones according to the needs of the refrigeration community. We also are working on improving the transport property predictions, on a new Helmholtz-energy-based mixture model, and on a graphical, easy-to-use, menu-driven front end.

The upgrade to NIST12 contains standard reference surfaces for methanol, toluene, and benzene, and the upgrade to NIST4 allows users an optional mass input mode in addition to the existing molar input mode. During the coming year we will provide a major upgrade to NIST4, containing new calculation options (isentropic and isenthalpic flashes), expanded table options, and an increase in database components to cover very heavy, tar-like hydrocarbon compounds.

We have been actively working on the new formulation for water recently adopted by the International Association for the Properties of Water and Steam (IAPSW) and are implementing the U.S. version of this new standard, including a graphical, menu-driven front end for the program; this version of NIST 10 will be ready for distribution in 1996. We have also completed development of a new dielectric constant formulation for water and are initiating work on new transport property standards.

This program is closely tied to numerous standards organizations. Results from this program have contributed to data projects of the AIChE DIPPR program, with which closer collaboration is being developed.

Publications:

Baltatu, M.E., Chong, R.A., and Huber, M.L., "**Viscosity of Defined and Undefined Hydrocarbon Liquids Using an Extended-Corresponding-States Model**", Int. J. Thermophysics 17, 213-221 (1995).

Friend, D.G. and Huber, M.L., "**Thermophysical Property Standard Reference Data from NIST**", Int. J. Thermophysics 15, 1279-1288 (1994).

11. Phase Equilibria in the Critical Region of Mixtures

***J.C. Rainwater**, D.G. Friend, A. Harvey, J.M.H. Levelt Sengers, J.S. Gallagher, and E. Lemmon (Univ. of Idaho)*

Objective: To develop models for the thermodynamics and phase behavior for mixtures in the critical region that are consistent with scaling-law behavior and non-classical critical exponents. To calculate critical and three-phase loci and critical-region phase equilibria and thermodynamics from traditional equation of state methods and to study their predictive power and shortcomings in the critical region.

Problem: Many important chemical processes occur in mixtures near critical conditions. Some of these include supercritical extraction with carbon dioxide and other solvents (where both solvent + heavy solute and solvent + entrainer mixtures must be understood), waste management methods with supercritical water, secondary recovery from petroleum reservoirs by carbon dioxide flooding, and the manufacture of low-density polyethylene plastics. Traditional equations of state, which lead to incorrect classical critical exponents, often either fail to converge or are inaccurate, particularly for coexisting densities, over an extended critical region. Therefore, there is a need for alternative thermodynamic models.

Approach: We have developed a scaling theory model, which explicitly incorporates non-classical critical exponents, to describe the critical region of mixtures. This approach is based on the work of Leung and Griffiths and was modified by Moldover and Rainwater. During the past several years, the model has provided highly accurate critical-region vapor-liquid equilibrium (VLE) correlations for many nonazeotropic and azeotropic binary mixtures. These include almost all mixtures that have been thoroughly measured for coexisting pressures, temperatures, compositions, and densities. The model has been extended to ternary and multicomponent mixtures, an extensive database of high-pressure VLE has been developed, and data from various unpublished theses have been presented in the literature together with correlations

and evaluations. The model has had some difficulty in correlating calorimetric quantities, but we have examined entropies and enthalpies with a generalized Clausius-Clapeyron equation and chemical potentials with a critical-region thermodynamic consistency test. Also, a number of closed-form asymptotic equations for the critical-region phase boundaries have been derived and tested against experimental data. The current emphasis is on extending the model to mixtures which display liquid-liquid equilibrium (LLE) in addition to VLE. Asymptotic formulations for the solubility properties of very dilute solutions in the critical region are also being extended, and the critical region for complex topologies is being studied with a classical extended-corresponding-states algorithm.

Results and Future Plans: During the past year, a successful non-classical model of a Type 2 mixture with VLE, LLE, and a three-phase locus has been developed. The model has been optimized to phase equilibrium data of the mixture carbon dioxide + methane, which does not directly exhibit LLE. There is convincing evidence, however, that when the system is cooled, the mixture would undergo liquid-liquid separation, except that the freezing transition interferes. As input to the correlation, we used experimental VLE data as well as low-temperature LLE isotherms generated from the classical extended-corresponding-states program NIST14. The non-classical model has been adjusted to agree closely with the calculated upper critical end point and LLE tie lines. It also agrees with all experimental bubble curves and most experimental dew curves, although a discrepancy remains on the dew side between 200 and 230 K.

A shortcoming of the approach for this and similar mixtures is that the VLE and LLE critical regions do not truly overlap, and the LLE critical locus is somewhat distant in thermodynamic space from the VLE critical locus. As an alternative, we are considering the crossover formalism of Kiselev and co-workers with separate critical regions and crossover functions for VLE and LLE. The model will be tested against mixtures with actual LLE data such as carbon dioxide + carbon disulfide and water + sulfur dioxide. A long-term project is to construct an analogous model of a Type 3 mixture with a discontinuous critical locus, which represents the extreme limit of immiscibility.

For dilute systems, an asymptotic formulation for the description of Henry's Law constants in the vicinity of the solvent's critical point has been extended in a semi-empirical correlation over a broad temperature range around the critical region. A new algorithm to calculate the critical locus has been introduced into a classical, extended-corresponding-states algorithm, and alternative methods to describe the critical region of Type 3 mixtures are being studied.

Publications:

Rainwater, J.C. and Lynch, J.J., "**A Non-linear Correlation of High-Pressure Vapor-Liquid Equilibrium Data for Ethylene + n-Butane Showing Inconsistencies in Experimental Compositions,**" Int. J. Thermophysics, 15, (1994), 1231-1239.

VanPoolen, L. and Rainwater, J.C., "**Vapor-Liquid Equilibria of Ternary Mixtures in the Critical Region on Paths of Constant Temperature and Overall Composition,**" Int. J. Thermophysics, 16, (1995), 473-481.

Gallagher, J.S., Friend, D.G., Given, J.A., and Levelt Senger, J.M.H., "**Critical Lines for Type III Aqueous Mixtures by Generalized Corresponding-States Models,**" Int. J. Thermophysics, 15, (1994), 1271-1278.

12. *Separation of Trace and Heavy Components from Natural Gas*

T.J. Bruno and K.H. Wertz (Univ. of Colorado)

Objective: Provide a reliable and efficient method of identifying and quantifying the heavier components of natural gas, especially in the C_6+ fraction. This will be achieved with an interactive database of standard chromatographic retention parameters that can be incorporated into the control software of laboratory and process gas chromatographs.

Problem: Natural gas is a complex two-phase (gas and liquid) mixture of organic and inorganic constituents, most of which are naturally occurring, but some of which are intentionally added during processing. The gas phase consists of approximately 40 major components and 175 minor constituents. The calorific or heating value of natural gas is usually determined from a mathematical model that requires the detailed composition of the gas as a basic input. The current industry practice of chromatographically determining the 32 most dominant species and backflushing the heavier fraction (above a carbon number of six) is inadequate, and is costing the gas industry millions of dollars per year. A great deal of information is simply discarded, since most of the heavier components are flushed out of the chromatograph without any analysis. The lack of standardization of an analytical procedure for these compounds prevents a detailed analysis from being performed. Funded by the Gas Research Institute, this project addresses the problem through the measurement of standard chromatographic retention parameters on six useful stationary phases.

Approach: We have approached the standardization and automation of the identification and analysis of the C_6+ fraction of natural gas by measuring standard chromatographic retention parameters as a function of column temperature for the most important stationary phases. The standard retention parameters include relative retentions, net retention volumes, and Kovats retention indices. The measurements are performed on a specially modified gas chromatograph that provides highly accurate retention measurements. These measurements are aided by specially developed methane marker vials and permeation vials that dispense sample and marker at infinite dilution. The column temperature dependence of these parameters are then modeled with an appropriate mathematical expression to allow prediction at all temperatures. These models are part of an interactive database that allows off-line identification, and optimization of more complex analyses.

Results and Future Plans: During FY95, we completed measurements of the retention parameters of approximately 60 fluids on three capillary column stationary phases at four column temperatures each (ranging from 60 to 140°C). The phases included a polydimethyl siloxane, a 5% phenyl polydimethyl siloxane, and a newly developed sol-gel column. These data are now in an interactive database that is under development. In the near future, we will complete measurements on three additional stationary phases of increasing polarity.

Publications:

Bruno, T.J., "**Permeation Tube Approach to Long Term Automatic Sampler Retention Index Standards**," J. Chromatography A 704, 157-162 (1995).

Bruno, T.J., "**Simple and Efficient Methane Markers for Chromatographic Samples**," J. Chromatography A (in press).

13. *Measurement and Modeling of Solubility in Supercritical Fluids*

***T.J. Bruno**, B.N. Hansen, A.F. Lagalante, R.J. Jacobson (Univ. of Colorado), and R.E. Sievers (Univ. of Colorado)*

Objective: Formulate a predictive model for solubilities of compounds in alternative solvents, particularly halocarbon compounds being developed as alternative refrigerants.

Problem: As a result of the Montreal Protocol chlorofluorocarbon (CFC) production phaseout, many industrially important chlorinated solvents used in cleaning and extraction processes will become obsolete. Replacements for the chlorinated solvents are likely to come from fully or partially fluorinated alkanes, ethers, or ketones which possess zero ozone-depletion potential. Unlike their chlorinated analogs, many of the fluorinated alternative solvents are gases under ambient conditions. Furthermore, the thermophysical properties of the fluorinated alternative solvents are such that these materials offer both conventional liquid extraction and the tunable solvent strength offered by near-critical and supercritical fluid extraction. Despite some successes using simple binary systems, serious limitations exist in equation-of-state modeling that use only physical properties of the solute and solvent to model supercritical and near-critical solute solubility. This is due to the often disparate chemical nature of the solute and solvent.

Approach: Modeling of solubility in the alternative solvents is being explored through the use of multivariate statistical analysis incorporating a number of empirical and thermophysical variables as input. Solubility data collected in the halogenated alternative solvents are found to be highly correlated to the functional groups of both the solvent and solute molecules. Work is in progress to extend significantly the empirically determined Kamlet-Taft solvatochromic chemical parameters to the alternative solvents in the subcritical and supercritical phases. In conjunction, chemical shifts from NMR measurements are being made that are indicative of binary interactions between the solvent and solute. Both chemical and physical variables will be incorporated into a multivariate statistical model to better predict solubility of industrially relevant compounds in the alternative solvents as well as provide insight into our understanding of the solution process itself.

Results and Future Plans: In recent years, we have designed and constructed numerous instruments for the quantitation of solubilities of solutes in subcritical and supercritical fluids. These include both dynamic methods and static-equilibrium-spectroscopic measurements. Solutes that we have studied range from classes of organometallic compounds to physiologically active natural products (β-carotene, capsaicin). During FY95, we obtained extensive solubility data for the metal β-diketonates and used those data to develop predictive models for the solubility based on the use of solubility parameters and intermolecular potential functions. Work is underway to construct a novel solubility measurement device based on magnetic levitation. This apparatus is now being designed.

The solubilities, as predicted from the multivariate statistical model, will be compared to the experimentally measured solubilities of specific solutes from our existing and developmental solubility measurement instrumentation. A predictive solubility model will suggest suitable alternative solvents and extraction conditions to substitute for an obsolete chlorinated solvent. Although initially the model will be tested using the pure fluorinated alternative solvents, it is envisioned that the model can be applied to other classes of solvents as well as to azeotropic mixtures of solvents.

Publications:

Lagalante, A.F., **"The Measurement, Modeling, and Applications of Metal β-Diketonate Complexes Dissolved in Supercritical Carbon Dioxide,"** Ph.D. Thesis, University of Colorado, Boulder, CO (1995).

Lagalante, A.F., Hansen, B.N., Sievers, R.E., and Bruno, T.J., **"Solubility of Copper (II) and chromium (III) Metal β-Diketonates in Supercritical Carbon Dioxide**," Inorganic Chem. 34, 5781-5789 (1995).

14. *Gas Sorption in Polymers for Separation*

J.J. Pellegrino, M.R. Yetzbacher, J. Tighe (Univ. of Colorado), and B.R. Mattes (Los Alamos National Laboratory)

Objective: This project addresses collection of quality data for sorption and transport of gases and vapors in industrially-significant polymers and for the development of quantitative structure/property prediction methods.

Problem: Although polymeric materials are used in membrane and adsorptive separation processes, a significant barrier to the development of new materials and optimum use of existing materials is the lack of *a priori* predictive capabilities for the solubilities and transport properties of mixtures in any selected polymer.

Approach: Measurements of gas and vapor sorption and diffusion in polymers are critical for development of techniques to predict transport properties. These measurements provide a means to study both chemical and structural subgroups of the polymer, and ultimately, to delineate rational design criteria for separations. Through our collaboration with Los Alamos National Laboratory, we have access to forms of polyaniline which appear to be examples of a newly emerging class of organic molecular sieve-type materials. This year we have also finalized a collaborative agreement with the National Research Council of Canada for provision of additional high-quality polymer samples based on meta-substituted polysulfones. Improved processes for obtaining high purity oxygen and nitrogen from air, upgrading natural gas, recovery of hydrogen from refinery gas at high pressure, water desalination, and recovery and purification of olefin streams are examples of important industrial uses of membranes.

Results and Future Plans: During the past year, data have been obtained for determining the film density and sorption and diffusion coefficient of oxygen in polyaniline films doped with HF or HCl. Also, two additional, fully-automated, sorption apparatus (based on pressure decay methods) have been designed and built. These instruments will provide improved accuracy for measuring unsteady responses at short times which are important for the meta-substituted polysulfones. An improved apparatus for measuring permeation time lag is being constructed. This apparatus uses a high accuracy, low flowrate (0-1 sccm) electronic flowmeter to measure the unsteady permeation response. When coupled to a mass spectrometer, it will provide transport properties of mixtures in selected polymers. With this apparatus we have thus far obtained pure component permeation data for helium, oxygen, and nitrogen in polyperfluorosulfonate films of 950 equivalent relative molecular mass. This material was provided by a commercial sponsor.

Publications:

Pellegrino, J.J. and Kang, Y.S., "**CO_2 /CH_4 Transport in Polyperfluorosulfonate Ionomers: Effects of Polar Solvents on Permeation and Solubility**," J. Membrane Science 99, 163-174 (1995).

15. *Adsorptive Separation Techniques and Fundamental Data*

***T.J. Bruno**, J.E. Mayrath, H.J.M. Hanley, F. Tsvetkov (Solar Dynamics, Inc., Israel), and C. Hampton (Univ. of Colorado)*

Objective: The goal of this research program is to provide the necessary infrastructural design data to allow efficient and effective adsorptive separations for process and environmental applications. Currently, adsorptive separation design is practiced industrially as a "black art", with a great reliance on intuition and significant overdesign of equipment and operating parameters.

Problem: Adsorptive separation techniques are a versatile and selective family of methods that are especially applicable to dilute solutions. This is a concentration regime that is particularly problematical and costly for many industries, including the energy sector, pharmaceuticals, and almost all phases of environmental remediation. Adsorbents are customarily characterized in terms of surface area and pore size distributions. These are intuitive concepts which do not adequately account for the actual structures and attractive potentials that increase concentrations of adsorbates (gases or dissolved materials) on the surfaces of adsorbents. Moreover, thermodynamic properties (such as isotherms and enthalpies) measured on "standard adsorbents" cannot fully account for porosity and adsorptive capacities for other adsorbates, nor can such measurements account for properties at conditions differing from those of the standard measurements. This situation makes the rational design of adsorptive separations nearly impossible.

Approach: This project consists of a data compilation effort and an experimental measurement and modeling effort. The data compilation work encompasses a literature review focusing on theory and measured data concerning adsorption from the gas phase on carbon, zeolites, and novel materials (polymers, urea, clathrates, etc.). Other physical property measurements of the adsorbents are correlated (where possible) with the customary or classical adsorption isotherms and areas and porosities. It is expected that some adsorbent structural parameters will emerge as more significant determinants of adsorption behavior. The current experimental effort concerns the enthalpy of adsorption of pollutants on unmodified clays and also clays modified with surfactants. We are using a chromatographic approach in which the clays (laponite, bentonite, montmorillonite, etc.) are deposited on glass spheres which are then packed into columns. These measurements build on our previous experience in the measurement of enthalpy of adsorption of polychlorinated biphenyls on gas pipeline surfaces. The temperature dependence of the specific retention volume provides the enthalpic information.

Results and Future Plans: The results of the literature review have revealed that there are no recognized or *de facto* standard adsorbents suitable for characterization. Adsorbent properties are known to vary from batch to batch, making correlations of measurements between batches highly uncertain. Data on a variety of adsorbates that can be traced to specific material lots or batches are scarce. This is unfortunate since this is the only data suitable for modeling and correlation development. Moreover, regeneration appears to change adsorbent characteristics, and few studies of characterization and physical properties as a function of adsorbent history are available. The Polanyi model was found to be adequate for carbon adsorbents provided the adsorbent-adsorbate system is well characterized and data at similar temperatures and adsorbate concentrations are available. Surface area and pore size distributions were found to be virtually meaningless for materials which are thought to provide material separation on the basis of size and/or shape.

Basic to understanding the structure of adsorbents is a knowledge of the skeletal density of an adsorbent. This quantity is the volume excluded to bulk vapor per unit mass of adsorbent. We are therefore in the final design phase of an apparatus to measure this important property. We plan a series of measurements of adsorbent weight in helium atmospheres at several densities and temperatures. We plan to extend this set of measurements to neon, argon, krypton, and xenon.

16. *Neutron and Light Scattering Studies of the Structure of Complex Fluids*

H.J.M. Hanley, C.D. Muzny, B.D. Butler, G.C. Straty, F. Tsvetkov (Solar Dynamics, Inc., Israel), S.K. Sinha (Argonne National Laboratory), and M.Y. Lin, M.W. Kim, and D.G. Peiffer (Exxon Research and Engineering)

Objective: Investigate the properties of micelles and their interaction with mineral surfaces, develop a metrology to characterize organic-inorganic nanocomposites, and relate the microscopic structure of composites to their mechanical and thermal properties.

Problem: Nanocomplexes made by polymerizing organic molecules attached to a mineral surface have considerable potential as lightweight materials with novel properties. A problem, however, is to exfoliate the mineral to achieve maximum bonding between the organic molecules and the mineral surface. In addition, the surface structure of an organic-inorganic complex needs to be better understood, since it controls the thermal and mechanical properties of the complex. Results from the program can be applied directly to environmental remediation and clean-up when using clay as the inorganic mineral.

Approach: We attempt to understand the structure of liquids and liquid/solid systems by neutron scattering using the SANS (small angle neutron scattering) spectrometers of the NIST Cold Neutron Research Facility, and by light scattering using the optical facilities of the Thermophysics Division at NIST, Boulder. Candidate materials were selected to be the clay mineral laponite and a surfactant synthesized by collaborators at Exxon. The surfactant is cationic and has a double bond that permits polymerization into a nanocomposite.

Results and Future Plans: We report on two aspects of the program: (1) clay platelet dispersion in a polymer matrix, and (2) the structure of worm-like micelles.

Polymeric composite materials are formed by embedding a high-modulus filler into a lower modulus matrix. The commercial and scientific potential of using clay as the filler is well appreciated and has received much attention recently, and it is known that the mechanical and thermal characteristics of a clay composite will be optimized when the largest possible clay surface area is presented to the matrix and fully integrated into it. To achieve this condition, the clay must be fully dispersed into its constituents – negatively charged platelets about 1 nm thick and 20 to 200 nm in diameter – and bonded to the matrix using an appropriate cationic organic intermediary. The reality, however, has been somewhat discouraging, because clay platelets tend to form large aggregates in the presence of organics. Hence, the corresponding composites fall short of the ideal. We have addressed the problem of clay platelet dispersion and have demonstrated a means to prevent clay aggregation by forming platelet-surfactant micelles. The precursor complex can be polymerized with a variety of standard monomers to form the composite. Here we discuss polymerization with acrylamide, and take the Exxon surfactant as the monomer. We have followed the synthesis of the material using dynamic (time-correlation) light scattering, and have investigated the polymer with x-ray diffraction, SANS, and electron microscopy. Our work suggests that, in general, novel polymeric composites of relatively low filler content, with novel properties, can be prepared and characterized. This will be explored further in the future.

Worm-like micelles have extremely interesting structures and properties. Although spherical at very low surfactant concentrations, they transform and undergo uniaxial growth to become worm-like cylindrical aggregates that can attain lengths of several hundred nanometers as the concentration is increased. With a salicylate as the counterion, their aqueous solutions are highly viscous and non-Newtonian at even moderate concentrations. Unlike a conventional polymer, however, the worms - sometimes called "living polymers" - break and reform continuously. The solution is thus stable when subjected to an extremely high mechanical stress, and its properties recover when the stress is removed. We have clarified the shape and growth pattern of the micelles using SANS data taken from a solution of the Exxon monomer under shear, and

light scattering data from the solution at rest. The structure of these micelles, when attached to a surface, will be a subject for future study.

Publications:

Lin, M.Y., Hanley, H.J.M., Straty, G.C., Peiffer, D.G., Kim, M.W., and Sinha, S.K., "**Small Angle Neutron Scattering Study of Worm-Like Micelles Under Shear**," Int. J. Thermophysics 15, 1169-1178 (1994).

Lin, M.Y., Sinha, S.K., Hanley, H.J.M., Straty, G.C., Peiffer, D.G., and Kim, M.W., "**A SANS Study of Worm-Like Micelles**," Physica B 213/214, 613-615 (1995).

Ottewill, R.H., Hanley, H.J.M., Rennie, A.R., and Straty, G.C. "**Small Angle Neutron Scattering Studies on Binary Mixtures of Charged Colloidal Particles**," Langmuir (in press).

17. Computer Simulation of Quenched Systems - Applications to Gelation

***H.J.M. Hanley**, C.D. Muzny, B.D. Butler, and D.J. Evans (Australian National Univ., Canberra)*

Objective: Investigate the mechanism of gelation and the structure of gels, develop a metrology to characterize gels, and relate the gel structure to its mechanical and thermal properties.

Problem: Gel technology is an essential factor in the preparation and fabrication of advanced materials. This task addresses the gelation of silica and related compounds. The problem is to relate the properties of the final gel to its microstructure which can, in principle, be altered at each step of the gelation process. In addition, the influence of an applied shear on the gelation mechanism and on the structure of the final gel should be explored to exploit the associated technological applications.

Approach: The approach is to carry out experiments on the scattering of radiation from the gels. Such experiments yield the structure factor, i.e., the microstructure, and complement the experiments by computer simulation of a model gel. In particular, we have argued that the mechanism of gelation has features in common with the phenomenon of spinodal decomposition.

Results and Future Plans: Dense silica gels, prepared from suspensions of 24 nm colloidal silica particles, have been studied by small angle neutron scattering. The measured scattered intensity increases at low wave vector, q, as the gelation proceeds, and the structure factor, S(q,t), of the final gel exhibits apparent power law behavior - usually interpreted as a signature of a long range network - provided the volume fraction of the silica is less than about 2/5 ($\phi \leq 0.18$) of close packing. The power law behavior, however, was observed at much higher volume fractions ($\phi \leq 0.30$) when the gelation occurred in the presence of an applied shear. To interpret the data in terms of the phenomenon of spinodal decomposition, we investigated the thermodynamic decomposition of a system of Lennard–Jones disks by non-equilibrium molecular dynamics. Thermostatted systems, unsheared and subjected to planar Couette

flow, were studied after temperature quenches into the gas-liquid and gas-solid coexistence regions. The systems displayed an interconnected particle cluster morphology after the quenches. The cluster growth was found to be temporally self similar, and S(q,t) obeyed the dynamic scaling relation $S(q/q_m(t)) = q_m(t)^{-d_f} \tilde{S}(q/\tilde{q}_m)$. Here, $q_m(t)$ is the location of the low angle peak in S(q,t), $\tilde{S}(q/\tilde{q}_m)$ is a time independent structure function, which peaks at $\tilde{q}_m$, and d_f is a fractal dimension. The behavior of the simulated structure factors has been compared to that in the gelling of dense silica suspensions, and there are striking similarities. This suggests that a characteristic fractal dimension of a gel may be determined from measurements of S(q,t).

Plans are to investigate the low-q peak in the structure factor which may be present in a gel, and to see how well the scaling law applies to neutron and light scattering data. Further simulations will be carried out to investigate possible differences between the mechanisms of spinodal decomposition and nucleation.

Publications:

Muzny, C.D., Straty, G.C., and Hanley, H.J.M., ***"Small Angle Neutron Scattering Study of Dense Sheared Silica Gels,"*** Phys. Rev. E 50, 675 (1994).

Butler, B.D., Hanley, H.J.M., Straty, G.C., and Muzny, C.D., "***Modeling of Neutron Diffraction Patterns from Sheared Silica Gels***," in Proc. Materials Research Soc., 376 (in press).

Muzny, C.D., Hansen, D., Straty, G.C., Evans, D.J., and Hanley, H.J.M., "***Simulation and SANS Studies of Gelation Under Shear,***" Int. J. Thermophysics 16, 337-346 (1995).

Butler, B.D., Hanley, H.J.M., Hansen, D., and Evans, D.J., ***"Dynamic Scaling in a 2D Lennard-Jones System Undergoing Gas/Solid Decomposition,***" Phys. Rev. Lett. 74, 4468-4471 (1995).

18. Finite Element Modeling of Fluid Dynamics and of Transport and Chemical Processes

G.R. Hardin, A.P. Peskin, J.D. Wolfe (Molten Metal Technology), and M.C. Jones (Colorado School of Mines)

Objective: Elucidate the physicochemical details of continuum fluid processes used in industrial applications to provide a basis for improved processes, to provide quantitative information for selection among processing alternatives, and to uncover limiting factors in current approaches.

Problem: Fluid/solid-particle systems are of great and growing importance in the process industries, with particulate solids representing well over half of the products. Processes include traditional separation technologies employing packed or fluidized beds, as well as many new applications in the production of advanced materials. Packed columns are used in many industrially important separation processes, such as distillation, adsorption, and chromatography. The packing provides large surface area for interphase mass transport and is critical to achieving desirable separation rates. Nevertheless, the interaction physics of packings with mobile phases is still not well understood, and it is difficult to characterize packings to adequately predict performance. For example, packed beds are often plagued by dead zones or channeling that degrade separation performance. Fluidized beds are used for diverse applications, including coal gasification, and for many catalytic systems where mass transfer is of serious concern, where catalysts must be frequently regenerated, or where tight temperature control is required. Many of the same issues facing packed-bed systems also occur in fluidized beds, including solids attrition, abrasion of pipes, and particle agglomeration. Many new applications of fluid/particle technology exist in which the goal is to create particles with a high degree of control of morphology or particle-size distribution. In addition to the data required for properties and their integration into process modeling, all of these types of fluid/particle systems are in great need of a fundamental understanding of fluid/particle physics to overcome existing performance barriers.

Approach: To address problems such as these, we have been developing a fluid dynamics and transport-phenomena software library for time-dependent modeling of momentum, heat, and mass transfer with homogeneous and heterogeneous chemical reactions. Into this library, we have incorporated new numerical techniques to model the motion of particles in a fluid. We will apply these new capabilities to study the basic physics of fluid/solid-particle systems.

Results and Future Plans: We have incorporated a new moving-boundary technique into our software to track the movement of multiple particles in a fluid. In this technique, particles are defined as distinct geometric entities (as opposed to simply being internal flow boundaries) within the numerical domain, and are allowed to move in time during a flow simulation. Initial applications of this method of geometric modeling will address flow distribution and channeling in packed beds for separation processes such as adsorption.

Publications:

Peskin, A.P. and Hardin, G.R., "**An Object-Oriented Approach to General Purpose Fluid Dynamics Software**," Computers Chem. Eng. (in press).

19. Measurement Services for Pressure, Vacuum, and Low-Flow Rate

P.J. Abbott, R.F. Chang, S.W. Doty, R.G. Driver, A.R. Filippelli, R.W. Hyland, R.F. Kayser, A.P. Miiller, C.R. Tilford, S A. Tison, and D.B. Ward

Objective: The Thermophysics Division provides calibration and special test services to a wide range of industries over extended ranges of pressure and gas flow (leak rate).

Problem: Pressure, vacuum and low gas flow measurements are critical to many industrial processes and research programs. In addition, verification of measurement accuracy is often required for exportation of U.S. manufactured equipment. To ensure the accuracy of industrial measurements and compatibility with international standards, national standards for pressure and vacuum are required.

Approach: The Thermophysics Division maintains primary standards and provides calibration services over a pressure range of 10^{-7} to 10^{9} Pa and gas flow standards over a range of 10^{-14} to 10^{-6} mol/s.

Results and Future Plans: Division calibration activities during the past year were comparable to the levels of previous years. Calibrations of piston gages remained at the 1994 level of 23 calibrated customer gages. The number of capacitance diaphragm gages calibrated increased from 32 to 37, while the number of spinning rotor gages and ionization gages calibrated increased to 30 from the 1994 level of 28. The number of leaks calibrated decreased from 16 to 12. In addition to calibrations provided to industry, the Thermophysics Division also performs many calibrations of gages for internal use at NIST to support critical measurements. This support has included calibration of helium leaks for the reactor, and calibration of pressure transducers used for flow measurements and fire research. Additionally, we have constructed and calibrated a low-pressure transducer package that will be used in a CCM-sponsored international intercomparison of pressure standards. The increase of calibration workload has been

accomplished through increased automation of the calibration services and increased efficiency in the reporting of results. Plans for FY96 include expansion of present low-flow calibration activities to flows as large as 10^{-4} mol/s (100 sccm).

Publications:

Filippelli, A.R. and Abbott P.J., **"Long-Term Stability of Bayard-Alpert Gauge Performance: Results Obtained from Repeated Calibrations Against the National Institute of Standards and Technology Primary Vacuum Standard,"** J. Vac. Sci. Technol. A 13, 2582-2586 (1995).

20. Quantitative Optical Measurements of UHV Pressures and Partial Pressures

J.P. Looney, R.D. van Zee, J.T. Hodges (836), and V. Simmons

Objective: To develop measurement standards for low-level gaseous contaminants in ultra-high vacuum systems, with particular emphasis on H_2O, CO_2, CO, O_2, H_2 and CH_4.

Problem: Low-level gaseous contaminants cause deleterious effects in UHV processing systems, e.g., semiconductor processing systems. Commercially available measurement instrumentation, which utilizes hot-filament electron-impact ionizers, perturbs the chemical composition in the vacuum system and therefore compromises measures of contaminant levels in UHV systems. More importantly, no standards exist for low-level gaseous contaminants in UHV systems because current vacuum standards are incompatible with chemically reactive or surface active species, such as water vapor.

Approach: Use high sensitivity laser spectroscopic techniques coupled with the unique low-pressure measurement capabilities of the Thermophysics Division to develop a quantitative measurement capability.

Results and Future Plans: Our initial focus has been on the development of quantitative measurement of H_2O densities, which is the most critical in terms of measurement need. We have focused our initial efforts on the development of a "realizable" water pressure scale, primarily for vacuum, and initially we have focused our efforts on the development of an H_2O pressure scale in the range ~1 kPa down to ~10^{-6} Pa using Cavity Ring Down Spectroscopy (CRDS). At present, it is our belief that it should be possible to develop a CRDS system with an H_2O sensitivity of 10^{-6} Pa or slightly better. The actual "best sensitivity" attainable will primarily depend upon two factors: the quality of the mirrors used to construct the cavity, and the laser system used to perform these measurements. During this past year we built a prototype CRDS system and undertook a series of experiments with

oxygen to delineate the important parameters in CRDS for quantitative number density measurement. It was determined that when all relevant experimental factors are properly accounted for, measurements of gas densities can be made with an imprecision of a few per cent. The results of the initial aspects of this work have been accepted for publication.

During the past year we have also conducted experiments to explore the feasibility of developing a quantitative measurement capability for water using resonance enhanced multi-photon ionization (REMPI). REMPI would operate over a more limited pressure range, but perhaps offer a lower ultimate detection limit. These experiments indicate a sensitivity at the level of $\sim 10^{-8}$ Pa.

Publications:

Hodges, J.T., Looney, J.P., and van Zee, R.J., "**Laser Bandwidth Effects in Quantitative Cavity Ring Down Spectroscopy**," Applied Optics (in press).

21. International Comparison of UHV Standards

A.R. Filippelli and C.R. Tilford

Objective: Establish the agreement between national ultra high vacuum (UHV) standards for pressures between 3×10^{-7} Pa and 9×10^{-4} Pa.

Problem: Several national standards laboratories maintain primary vacuum (pressure or gas density) standards for pressures as low as 10^{-7} Pa. However, comparisons of these standards have been restricted to pressures of 10^{-5} Pa and above. The increasing importance of the UHV range for industrial and scientific activities makes it desirable to insure that the different standards agree to within their combined uncertainties.

Approach: A comparison of national UHV standards has been organized by the Low-Pressure Working Group (chaired by C.R. Tilford) of the Consultative Committee for Mass and Related Quantities. The PTB (Physikalisch-Technische Bundesanstalt, Berlin) agreed to serve as pilot laboratory and supply the transfer standards - two ionization gages. A first-phase comparison has been carried out between the three laboratories with the largest volume of vacuum calibrations: NIST, the National Physical Laboratory, Teddington (NPL), and PTB.

Results and Future Plans: The first-phase measurements have been completed and analyzed. The results are compromised by instabilities of the transfer standards, resulting in larger-than-expected uncertainties for the comparison measurements, and forcing their analysis as two bilateral comparisons: NIST-PTB and NPL-PTB. The NIST-PTB results for the two ionization gage transfer standards (Bayard-Alpert and extractor ionization gages) are shown in the figure. The error bars represent the two-sigma uncertainties of the comparison results, the tolerance lines are the combined two-sigma uncertainties of the NIST and PTB standards. As can be seen, the measured differences are well within the combined uncertainties of the two standards and the measurement results. Further, the results for the two independent transfer standards are essentially uncorrelated (correlation coefficient

= 0.09) so that the results can be further summarized by the average of the measured differences, (-0.23 ± 0.20)%.

The NPL-PTB comparison was much less satisfactory; the results for the two transfer standards were not highly consistent, but did indicate differences between the standards as large as 5% or 6% at the lowest pressures, well outside the combined uncertainties of the standards. Given the good agreement between the NIST and PTB standards, it is reasonable to assume similar differences between NIST and NPL.

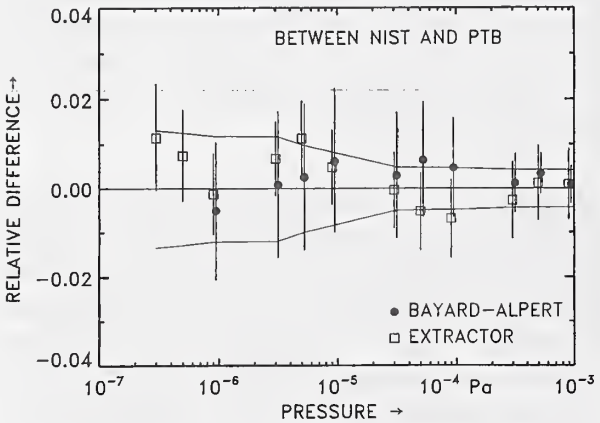


Figure 1. Indicated differences between NIST and PTB standards for two independent transfer standards.

A manuscript reporting the results to date has been prepared and is being reviewed within each of the three laboratories. At the same time, preparations are being made to repeat the NPL-PTB measurements in early 1996. When this issue is resolved, the comparison will be extended to other national laboratories.

22. *Measurements and Standards for the Metering of Low Gas Flows*

S.A. Tison and C.R. Tilford

Objective: To develop primary flow standards in the range 10^{-7} to 10^{-3} mol/s and to transfer this flow measurement capability to U.S. industry, government, and academic institutions.

Problem: Many industrial processes require the accurate metering of mass flow over the range of 10^{-7} to 10^{-3} mol/s. In particular, the SEMI/SEMATECH Mass Controller Working Group identified the need to measure flows in this range with uncertainties of 1% or less and identified the need for national flow standards with uncertainties of 0.2% or less. National standards for flow in this range are not adequate to meet the identified industrial requirements.

Approach: The Thermophysics Division initiated a program to develop primary flow standards which would operate over the range 10^{-7} to 10^{-3} mol/s with uncertainties of 0.1% or less. To transfer this measurement capability to industrial users, the properties of commercially available flow meters will be investigated and the development of highly repeatable flow meters will be explored.

Results and Future Plans: A constant volume primary flow meter was constructed which operates over a range of 10^{-9} to 10^{-3} mol/s with uncertainties of 0.1% or less. This system utilizes two accumulation volumes, 2 liters and 150 liters, in conjunction with high accuracy pressure and temperature instrumentation to calculate the change in mass in the volume when a flow is introduced. The system is of all metal construction with high vacuum type fittings and is compatible with all non-corrosive gases. This system was compared with existing flow standards in the Thermophysics Division over their overlapping ranges of 10^{-8} to 5 x 10^{-6} mol/s. The two standards agreed to within their two- sigma respective uncertainties of ±0.1%.

Five commercially available thermal mass flow meters (TMFMs) from five different manufacturers were characterized to determine their operational uncertainties and metrological attributes. Two of

the five tested TMFMs were significantly outside of their manufacturer's ascribed uncertainty of ±1% (7% and 17%). The TMFM's were determined to be stable to within ±1% over a one year period. The NIST measured gas correction factors for these instruments differed from the manufacturer's reported values by as much as 18%.

An ultra-stable laminar flow meter was developed which uses pressure differentials as large as 0.8 MPa to generate flows over a range of 10^{-6} to 10^{-3} mol/s. This instrument is still under development but initial data indicates it may have a long term repeatability of ±0.1%.

In FY96, a constant pressure flowmeter which operates over a range 10^{-7} to 10^{-3} mol/s will be developed. An intercomparison of flow standards between the Process Measurements Division and the Thermophysics Division over the range of 10^{-4} to 10^{-3} is planned. Collaborations with industrial consortia, such as SEMI/SEMATECH, will be pursued to transfer the new NIST flow measurement capability to U.S. industry.

This work is funded in part by the National Semiconductor Metrology Program (NSMP).

Publications:

Tison, S.A., **"Improved Gas Flow Measurements for Next-Generation Processes,"** in Semiconductor Characterization - Present Status and Future Needs, Edited by W.M. Bullis, D.G. Seiler, and A.C. Diebold, AIP Press (in press).

Tison, S.A., **"A Critical Evaluation of Thermal Mass Flow Meters ,"** J. Vac. Sci. Technol. (in press).

23. Characterization and Optimization of Residual Gas Analyzers for Semiconductor Processing

M. Li (College of William and Mary), P.J. Abbott, C.R. Tilford, and S.A. Tison

Objective: Characterize and improve the metrological properties of residual or partial pressure analyzers (RGAs or PPAs), and develop *in situ* calibration techniques for processing applications.

Problem: Residual gas analyzers have been widely used for qualitative vacuum system diagnostics. The increasing complexity of semiconductor processing has generated a further need for real-time process monitoring, typically to monitor gaseous contaminants or for process control. Both of these require quantitative measurements if they are to be successful in a large-scale manufacturing environment. However, the quantitative capabilities of most RGAs are not adequate for these tasks. There are needs to better understand these instruments, to improve their performance, and to ensure consistent results by providing the users with access to national standards.

Approach: To determine critical performance parameters, optimum operational conditions, and instrument design improvements, we will acquire quantitative test data for commercial RGAs and develop generic RGA operation models. We will develop *in situ* calibration techniques to transfer the NIST vacuum standards capabilities to users.

Results and Future Plans: During the past year, efforts concentrated on the development of an automated RGA calibration system, which was used to continue our testing of quadrupole RGAs, and the development of a model to predict the dependence of quadrupole RGA sensitivity on pressure, which is the major factor limiting RGA performance in typical semiconductor processing applications. The automated calibration system has functioned very well, and we believe the design and implementation can be simplified and adapted for *in situ* use in industrial process chambers. Laboratory testing focused on resolving questions raised by earlier test results, evaluating new models of quadrupole

RGAs, and validating the predictions of the performance model. Of particular note were the results for a new miniaturized RGA that exhibits constant sensitivity to pressures two or three orders of magnitude higher than observed for conventional RGAs. The encouraging results for this instrument, which is relatively new to the market and still evolving, are tempered by inferior mass resolution and sensitivity, which may limit its use for many applications.

A model was developed to predict the high-pressure performance of quadrupole RGAs. This model calculates the effects of ion space charge in the transition region between the ionizer and the quadrupole filter, and within the filter itself, on the instrument sensitivity. For high-pressure, high-space-charge operation, it predicts a loss of ions, and a corresponding decrease of RGA sensitivity, due to beam spreading beyond the "acceptance aperture" of the quadrupole filter. These results are in qualitative agreement with most of our experiment data. The model also predicts that the effects of ion space charge can be minimized, and RGA linearity improved, by increasing the ion energy and/or minimizing the ion flight path. These predictions are in good agreement with experimental data and explain the superior linearity observed for the miniature RGA. The model further predicts that space charge effects can be important even within the quadrupole filter, which explains some previous "anomalous" experimental results. In FY96, we plan to continue testing to validate other predictions of the space-charge model for quadrupole RGAs. We will also test a time-of-flight RGA to see if this type of instrument avoids some of the generic defects of quadrupole instruments.

24. Development of New Calibration Service for High-Pressure Gas

S.W. Doty, C.D. Ehrlich, R.F. Kayser, and S.A. Tison

Objective: To develop transfer standard piston gages which are capable of measuring gas pressures up to 110 MPa with uncertainties of 100 ppm or less.

Problem: The availability of NIST calibration services for gas pressures to 110 MPa is required by customers in the U.S. military and in industry. However, prior to FY95, NIST provided services between 10 and 110 MPa only for oil, and this capability was not easily transferable to a gas-operated system.

Approach: (1) To investigate two commercially available gas-oil dividers, (2) to use current NIST oil pressure standards to calibrate two gas piston gages using the selected gas-oil divider, and (3) to use these two gas piston gages as standards for a gas calibration service up to 110 MPa.

Results and Future Plans: Two commercially available gas-oil dividers were investigated to determine their suitability for our task. The first had a direct gas-oil interface and used a sight glass to determine the level of the interface. The second used a metal diaphragm and nulling electronics as a separation partition between the two media. It was determined that the direct gas-oil interface introduced a number of effects into the comparison process which were not desirable. Chief among these were the solution of the gas in the oil, which changed the oil density and took hours for equilibration. The metal diaphragm, once appropriately calibrated, served as an adequate separator.

With the metal-diaphragm separator, a high-accuracy oil piston gage (PG41) was used to calibrate two gas operated piston gages over the pressure range 10 to 110 MPa. The gas piston gages are commercially available instruments which are of considerably different design and manufactured by independent companies. Both instruments performed well over the tested pressure range. The

gas operated piston gages were determined to have uncertainties in their measured pressure of approximately 39 ppm (two standard deviations). A calibration service for high pressure gas calibrations up to 110 MPa has been initiated. This project was funded by the Department of Defense Calibration Coordination Group.

25. Primary Acoustic Thermometry at High Temperatures

D. Ripple (836), M.R. Moldover, and K.A. Gillis

Objectives: (1) To reduce the uncertainty in the determination of the thermodynamic temperature by a factor of 3-8 in the range from 500 K to 900 K using as a primary standard speed-of-sound measurements in low-density argon, and (2) to improve the accuracy of the high-temperature fixed points (e.g., tin point, zinc point) and radiometry tied to these fixed points.

Problem: The most accurate determinations of thermodynamic temperature above 700 K use relative radiance measurements referenced to a black body near 700 K. The thermodynamic temperature of the black body is known from NIST constant volume gas thermometry (CVGT) experiments. Unfortunately, two NIST CVGT experiments differ from each other for reasons that are not well understood. The difference leads to an estimated uncertainty of 13 mK in temperatures near 700 K and 50 mK in temperatures near the gold point (1337.33 K).

Approach: We shall measure the frequencies of both acoustic and microwave resonances in a spherical, argon-filled cavity bounded by a thick, metal shell which in turn will be enclosed by a high-performance thermostat. The data will determine the speed of sound in the argon from which the thermodynamic temperature will be deduced. The temperature will be transferred to platinum resistance thermometers and then to fixed-point devices. For acoustic thermometry, the measured quantities are frequencies and the temperature. This contrasts with CVGT which requires the measurement of pressures and temperature; thus, systematic effects will be very different in the present work and may resolve the discrepancies in the CVGT.

Results and Future Plans: A significant technical challenge will be to guarantee the purity of the argon within the resonator. To accomplish this, clean argon will slowly flow through the resonator. Throughout the measurement cycle, the pressure of the flowing gas must be stable to 1 part in 10^6 in the

range 50 - 500 kPa. During FY95 we developed a novel flow controller that varies the flow impedance of a stainless-steel capillary tube by heating the tube electrically. We demonstrated the required pressure stability in a flowing gas at ambient temperature. During FY96, a spherical cavity will be set up together with a gas handling system. They will function as a test bed for studying the influence of flow on the resonance measurements and for characterizing transducers at ambient temperatures. During FY96, we shall complete the final designs for the high-temperature resonator and the high-performance thermostat.

Another technical challenge will be to develop electro-acoustic transducers that are compatible with the high temperatures and which neither contaminate the argon nor significantly perturb the resonance frequencies. The "thermophone" effect will be used as a sound source. Sound will be generated either by modulated light transmitted into the cavity or by electrically heated microfabricated resistors. As sound detectors, we are evaluating high-temperature versions of commercial capacitance microphones as well as detecting the motion of a thin diaphragm using either optical interferometry or radio-frequency impedance measurements. During FY96 these approaches will be tested until a successful one is selected. A back-up plan is to use acoustic wave guides to couple sound between the resonator and external sources and detectors at ambient temperature.

26. *Advanced Refrigerators for Cryogenic Applications*

***R. Radebaugh**, P.E. Bradley, E.D. Marquardt, M.A. Lewis, J. Gary (CAML), A. O'Gallagher (CAML), F. Kuriyama (Ebara Corp., Yokohama, Japan), T. Kuriyama (Toshiba, Kawasaki, Japan), J.H. Xiao (Chinese Academy of Sciences, Beijing), and C. Walther (Universität Dortmund, Germany)*

Objective: Develop new refrigeration techniques and improved refrigerator components for the temperature range of 120 K and below. Investigate and use measurement and modeling techniques for evaluating performance of cryocoolers and their components, such as heat exchangers.

Problem: Cryocoolers are required for many technology areas, including the cooling of infrared sensors for surveillance and atmospheric studies, the cooling of superconducting electronics and magnets, the cooling of cryopumps for clean vacuums in semiconductor fabrication processes, the liquefaction of natural gas for clean-burning transportation fuel, and many other existing or potential applications. The use of these technologies has been hampered because of problems with existing cryocoolers. These problems include short lifetimes, inefficiency, high cost, and excessive vibration. Improved cryocoolers would stimulate the growth of all these technology areas.

Approach: Precision moving parts in existing cryocoolers are a source of wear, vibration, and high cost. Our approach in the development of improved refrigeration processes has been to eliminate most or all moving parts while still maintaining high efficiency. We have focused much of our research on pulse tube refrigerators, which have no cold moving parts. Some applications are now using a recent joint invention of NIST and Los Alamos National Laboratory (LANL) called a ThermoAcoustically Driven Orifice Pulse Tube Refrigerator (TADOPTR) that produces cryogenic temperatures with no moving parts in the entire system. Mechanically driven pulse tube refrigerators, which have one moving part at room temperature, are more applicable where size and efficiency are most important. Experimental and

theoretical work at NIST on the behavior of pulse tube cryocoolers and their components yielded efficiencies as high as those obtained with the Stirling cryocooler, which has two moving parts but has been the most efficient of all cryocoolers. Further research is necessary to improve lifetimes and to reduce cost of the pulse tube cryocooler for use in many applications. Our studies encompass measurements and modeling of losses to further improve efficiency while increasing lifetimes and simplifying construction techniques. NIST research in this area has industry and other government agency support to aid in the transfer of this technology.

Results and Future Plans: During FY95, we completed construction of an apparatus to measure the thermal conductance of stacked regenerator materials, such as stacked screens, as a function of packing pressure. Almost no data exist for the thermal conductances of these stacked materials, but they are needed for the optimum design of regenerative heat exchangers in many types of cryocoolers, including the pulse tube refrigerator. Measurements of the thermal conductance of several materials and geometries will be performed next year and used to develop a model to predict the thermal conductance.

A three-stage pulse tube refrigerator designed for operation down to 4 K was constructed in FY95. A temperature of 8 K has been achieved. Problems were found in the second-stage regenerator and pulse tube. Modifications to these components will be made next year in an attempt to reach 4 K. Refrigeration at these low temperatures is needed for cooling conventional low temperature superconductors, such as those used in Josephson-junction voltage standards. This refrigerator will be used to study the behavior of regenerators and pulse tubes in the low temperature region where nonideal gas effects are significant.

Under a CRADA with Cryenco, Inc. of Denver, CO, we have designed and collaborated on the construction and testing of the world's largest pulse tube refrigerator. It is designed to liquefy 1500 L/day of natural gas for use with fleet vehicles that operate with natural gas. This first version uses a mechanical compressor, but the goal is to drive the pulse tube with a thermoacoustic driver that has been designed at LANL. Such a liquefier with no moving parts is needed for small liquefaction plants where reliability is important and capital costs must be kept low. Tests so far have shown that natural gas could be liquefied in the system, but that an excessive pressure drop in the cold heat exchanger needs to be corrected to produce liquid at the desired rate.

We have collaborated with Lockheed Martin of Palo Alto, CA, under several contracts this past year. They are interested in using pulse tube refrigerator technology in aerospace and commercial applications. This technology-transfer activity involved designing, constructing, and testing an 80 K single-stage pulse tube cryocooler that had a unique coaxial geometry for compactness. A 60 K two-stage pulse tube cryocooler was also designed and constructed for Lockheed Martin. This cryocooler will be tested in FY96 and delivered to Lockheed Martin.

Publications:

Bradley, P.E. and Radebaugh, R., "**A Three Stage Pulse Tube Refrigerator for Temperatures Near 4 K,**" Adv. Cryo. Eng. (in press).

27. *Development of a Cryogenic Catheter*

***R. Radebaugh**, E.D. Marquardt, M.A. Lewis, M.L. Huber, and J. Dobak (CryoGen, Inc.)*

Objective: To develop a simple catheter technique to replace much more costly and dangerous surgical techniques currently practiced; more specifically, to determine the feasibility of achieving a temperature down to 120 K at the tip of a 1 m long, 3 mm diameter catheter with enough cooling power to freeze about 1 g of tissue in the heart to eliminate heart arrhythmias.

Problem: The cryogenic catheter is to be inserted into the large vein leading from the leg to the heart. This vein has a sharp bend just above the heart which requires that the catheter be quite flexible. Since cryoablation of tissue is to occur only at the tip, only the tip is to be cooled to 120 K, and the remaining length must be warm enough to prevent freezing. Current cryogenic medical probes that use liquid nitrogen must be vacuum insulated and are rigid. For safety purposes the maximum pressure that can be used for any fluid in the catheter is about 3 MPa (420 psia). For medical reasons, the catheter must be disposable, and therefore of low cost.

Approach: This research has been carried out under a CRADA with CryoGen, Inc. (formerly Aegis Medical Technologies). The flexibility and small diameter requirement prevented us from using the forced flow of liquid nitrogen, since the entire length of the catheter would then need to be insulated and become too large and stiff. We chose to use a Joule-Thomson refrigeration process in which cooling is produced when a high pressure fluid expands to low pressure. The high pressure fluid flows through a 1 mm diameter tube inserted coaxially inside the 3 mm diameter tube in which the returning low pressure fluid flows. To achieve 120 K with a high pressure limit of 3 MPa, pre-cooling of the high pressure stream inside a miniature heat exchanger at the tip of the catheter is necessary. An optimized fluid mixture provides more refrigeration than a pure fluid, so such a mixture needed to be identified based on the thermodynamic properties of fluid mixtures.

Results and Future Plans: The thermodynamic properties of various gas mixtures were determined using the computerized databases NIST4 and NIST14, which employ an extended-corresponding-states model for calculation of mixture properties. These programs were modified to automatically search all possible combinations of fluids that had freezing points below 115 K and provided the maximum refrigeration per unit of heat transfer in the heat exchanger. Initially a five-component mixture of nitrogen and various hydrocarbons was identified from NIST14. Later, with the use of NIST4, other mixtures were identified that were not flammable and contained no serious ozone depleting fluids. These new mixtures also had superior thermodynamic properties. The fluid mixtures identified for use in the catheter existed in the two-phase region over most of the temperature range between 120 and 300 K. No data existed on the heat transfer coefficients of such mixtures, and their existence in the two-phase region produced even more uncertainty in the heat transfer coefficients. Using estimates of the heat transfer coefficients, we designed a miniature heat exchanger of 2.5 mm diameter and 5 mm length. These heat exchangers could be stacked in series, if needed, to provide additional heat exchange area. The fabrication process was based on its capability to yield several hundred heat exchangers simultaneously to satisfy the need for low cost. The process proved satisfactory, and tests were made with various heat exchangers with different dimensions. The best results were obtained with a stack of 3 heat exchangers for a total length of 15 mm.

After several tests, and with some precooling of the high pressure stream to about 0°C before entering the inner tube of the coaxial catheter, a minimum temperature of 85 K was achieved at the tip of the catheter when exposed to ambient air. The maximum pressure used for these tests was only 2.5 MPa. Preliminary measurements of the refrigeration power at the tip showed about 3 W at 140 K. To freeze 1 g of tissue in the presence of blood flow in the heart, CryoGen estimates that a refrigeration power of about 10 W at 150 K is required.

Future work will involve further measurements of the refrigeration power with various heat

exchangers and fluid mixtures. Measurements of heat transfer coefficients are needed to further improve the heat exchangers. We are transferring the technology to CryoGen to enable them to make such catheters for animal tests in about a year. If those tests prove satisfactory, CryoGen will file application to the FDA for approval to use such catheters in humans.

Publications:

Dobak, J., Radebaugh, R., Huber, M.L., and Marquardt, E.D., "**Miniature Mixed Gas Refrigeration System**," Patent No. 95-041 (issued October 12, 1995).

28. Cryogenic Flow Measurements

J.L. Scott, J.D. Siegwarth, and M.A. Lewis

Objectives: (1) To provide the National Standard for the measurement of liquid nitrogen flow, and (2) to assist NASA in the evaluation of measurement techniques for liquid oxygen flow to the Space Shuttle main engine.

Problem: (1) An uncertainty analysis of the liquid nitrogen flow calibration facility in 1994 revealed an increase in the random variation of the load cell whose output is used to compute the mass of liquid nitrogen accumulated during a calibration point. In addition, much of the associated structure of the flow facility was old and in need of refurbishing and/or improvement: wiring, vacuum jacketing, and piping configurations. (2) Liquid oxygen flow to the Space Shuttle main engine occurs at very high velocities. The low temperature and high velocity conditions limit the choice of flow measurement techniques to those that are very durable. Existing ultrasonic flow meters have experienced failures in this application, but the cause for these failures is unkown.

Approach: (1) An effort was undertaken to improve the accuracy and reliability of the flow facility and to enhance its flexibility so that future improvements and expansions could be accomplished with greater ease. In particular, a new load cell with improved uncertainties was purchased and installed, and all of the wiring associated with the load cell was replaced. New, modular vacuum lines were also installed, and piping configurations both upstream and downstream of the test section were improved. (2) Some of the conditions that occur in high-velocity liquid oxygen flow will be simulated using a high-velocity gas flow. The durability of a gas meter will be tested in these simulated conditions.

Results and Future Plans: (1) The liquid nitrogen flow facility should be operational early in 1996, and after a reassessment of the uncertainty, tests will be conducted for two companies currently in the queue for meter testing and/or calibration. (2) A new preamplifier for the high velocity gas flow meter was constructed and tested. The durability of this meter will be investigated in FY96.

VI. Analytical Chemistry Division (839)

Willie E. May, Chief

A. Division Overview

The Analytical Chemistry Division serves as the Nation's Reference Laboratory for chemical metrology to enhance U.S. industry's productivity and competitiveness, assure equity in trade and provide quality assurance for chemical measurements used for assessing and improving public health, safety and the environment. The skills and knowledge derived from laboratory-based research concerning the phenomena that underpin the measurement of chemical species in a broad spectrum of matrices are applied to the development and critical evaluation of measurement methods of known accuracy, precision, sensitivity, and selectivity. The resulting reference methodology is used in a highly leveraged manner and serves as the foundation for the certification of chemical composition in more than 850 Standard Reference Materials important to U.S. industry, government agencies, and educational institutions. Measurement methods derived from Division research activities are also used for establishing and maintaining chemical measurement traceability links for commercial reference materials producers and measurement comparability links with chemical metrology laboratories world-wide. The Division's FY95 budget was approximately $13M of which about $6M was from other Federal and State Government Agencies and American Industry for research and/or measurement services provided on a cost reimbursable basis.

Formerly, many of these activities were carried out in two separate Divisions. In the fall of 1994, the inorganic and organic analytical functions were combined to form the Analytical Chemistry Division. During FY95, the Division was organized into eight Groups: Analytical Sensors and Automation; Atomic and Molecular Spectrometry; Electroanalytical Research; Gas Metrology; Inorganic Mass Spectrometry; Organic Mass Spectrometry; Nuclear Methods; and Separation Science.

During the past year, the research and service activities within the Division have been realigned into five Groups:

- Spectrochemical Methods
- Organic Analytical Methods
- Gas Metrology and Classical Methods
- Chemical Sensing and Automation Technology
- Nuclear Methods

This restructuring will establish a basis for more coherent and synergistic programs in chemical metrology and reference materials development, for providing advice and measurement services to other government agencies, scientific organizations and U.S. industry, and for bench marking with other National Metrology Laboratories. Details concerning the Divisions primary research and service activities are provided below on a group by group basis.

Spectrochemical Methods

Research activities in this area are focused on the development, critical evaluation and application of methods for the identification and measurement of inorganic chemical species using x-ray, optical and mass spectrometries. Research in Isotope Dilution Mass Spectrometry (IDMS) includes the development of procedures and instrumental modifications for negative ion MS to determine Re, Os, and Cl. These species are pivotal in certain chemical systems used for dating geologic samples. Other research is directed toward improving the efficiency and ease of analysis, taking advantage of new approaches for preparation of the sample prior to analysis. For example, a commercially available continuous flow microwave digestion system has been tested as a means to insert the isotopic spike, digest the sample, and effect isotopic equilibration for IDMS. Under a CRADA with the CEM Corporation, this system was proven to reliably automate these functions resulting in a highly

accurate determination of lead in a candidate lead in paint/dust reference material [SRM 2583].

Research in X-Ray Fluorescence (XRF) and optical methods includes applications of direct solids injection into the graphite furnace for electrothermal Atomic Absorption Spectrometry (AAS) and small particle analysis using energy dispersive XRF. We are also studying the application of Glow Discharge Optical Emission Spectroscopy (GDOES) for surface analysis mapping of samples up to 15 cm on a side. Further work in GDOES will examine the feasibility of depth profiling of elemental species and mapping of non-conductive samples using a radio-frequency discharge source. The high-accuracy identification of spectral wavelengths in plasma sources used by analytical chemists has been the subject of ongoing research. Drs. John Travis, Michael Winchester, and Marc Salit along with two non-NIST co-authors were awarded the Spectrochimica Acta Atomic Spectroscopy Award for their paper on UV/Visible Fourier transform spectroscopy noise cancellation. This paper was recognized by the editorial board as the most significant contribution to spectroscopy published in the journal in 1993. During the past year, this team along with scientists from the NIST Physics Laboratory used a UV/Visible Fourier Transform Spectrometer referenced to a clock frequency to identify a 6 parts in 10^8 bias in the wavelength assignment for the "green line" in the mercury spectrum. This standard line has been used over the years to calibrate spectra used in chemical metrology and for assignment and calculation of atomic energy levels for several other elements. The system is currently being used to re-measure mercury spectrum as well as other important reference spectra.

The very high accuracy and precision afforded by IDMS are exploited to analyze reference materials intended for use as calibration standards for other methods. IDMS has recently been used in this mode to determine important elements in clinical reference materials such as **Human Serum** [SRM 909b] resulting in the certification of electrolytes (e.g., Ca, Cl, K, and Mg) with total uncertainties significantly less than 1% relative. This serum-based material is used by the world-wide clinical community for establishing an NIST traceability link for important health-care diagnostic markers. Certification efforts using spectrochemical analysis methods such as Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), AAS, non-IDMS versions of ICP-MS, and XRF spectrometry are directed toward problems requiring accuracies for trace elements of 1-5% relative. Reference materials such as industrial sludge, petroleum coke, powdered paint, and household dust have been analyzed using these methods. Several elements in **Trace Elements in Water** [SRM 1643d] and **Natural Water** [SRM 1640] were also determined by ICP-MS during the past year.

The certification of powdered paints, dusts, and two soil reference materials is sponsored by Environmental Protection Agency (EPA) to support the reduction of lead contamination in the U.S. Recently, we have also used ICP-MS, XRF, and AAS to determine the reference values for a 19-element batch of wear metal in oil calibration standard. This material is used by the Joint Oil Analysis Program in Department of Defense (DoD) to ensure quality and traceability for its oil analysis world-wide. Traceability infrastructural activities also include the determination of critical trace elements in a new Antarctic Sediment Material, which is being certified by an international effort coordinated by the Italian government. NIST is also responsible for drafting and conducting the second international intercomparison of inorganic analysis under the auspices of the Consultative Committee for Amount of Substance for the International Committee for Weights and Measures.

Organic Analytical Methods

Activities within the group are directed toward the development, critical evaluation, and application of methods for the identification and measurement of organic and organometallic species. Currently, laboratory research activities are focused on organic mass spectrometry and separation techniques including gas chromatography (GC), liquid chromatography (LC), supercritical fluid chromatography (SFC) and extraction (SFE), and capillary electrophoresis (CE).

Recent activities in organic mass spectrometry have focused on the development of electrospray ionization mass spectrometry as a tool for the

quantitative determination of proteins in biological matrices. A method for the mass spectrometric determination of albumin (MW 65K daltons) in serum has been developed and is being critically evaluated. We are currently working toward establishing reference methods for other important biomarkers such as glycohemoglobin, an important marker for diabetes and creatine kinase MB, and a marker for acute myocardial infraction. We have also completed preliminary work on a method for serum thyroxine, an important marker for thyroid function as part of our ongoing collaboration with the College of American Pathologists (CAP) to establish definitive methods for clinically significant species.

Recent activities in separation science have focused on investigations of the physical and chemical processes that influence the separation and detection of organic and organanometallic species and the application in the development of reference methods for the determination of organic species in natural matrices. In the area of separations, we are investigating the molecular interactions that influence chromatographic retention with particular emphasis on the design of stationary phases for specific applications in LC, GC, and SFC. In LC, our recent efforts have focused on new approaches for the synthesis of alkyl-bonded stationary phases with emphasis on the preparation of C30 and longer alkyl chains specifically tailored for the difficult separation of β-carotene isomers and other carotenoids of interest in health and food/nutritional studies. A new research effort in chiral separations has been initiated. Current research is focused on developing SFC separation strategies for optical isomers of pharmaceutical and agricultural interest where we are finding that SFC provides significant advantages over the LC-based methodologies currently used. Research is also being conducted in organometallic "speciation." A reference method based on gas chromatography with atomic emission detection for methylmercury in marine tissue has been developed and validated and is being used to provide the first NIST-determined values for methylmercury in several marine environmental SRMs.

Several new SRMs are being developed to support measurement activities in the environmental, health-care, food, and nutritional labeling communities. Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated pesticides, and methylmercury are being certified in a marine sediment and three mussel tissue materials to support marine environmental monitoring efforts. A new **PAHs in Diesel Particulate** material [SRM 1975] was developed to provide an accuracy benchmark for both the chemical measurements and Ames bioassay communities. Measurements were completed for the certification of clinical analytes in SRM 909b, **Human Serum**. This material is used by the clinical community to establish an NIST traceability link for important health-care diagnostic markers such as cholesterol and triglycerides [heart disease], glucose [diabetes], urea and creatinine [kidney function], and uric acid [gout]. A renewal of our **Fat-Soluble Vitamins and Carotenoids in Human Serum** material [SRM 968b] was completed and the development and certification of an **Infant Formula** [SRM 1846], a **Baby Food Composite** [SRM 2383], and a **Human Diet Composite** [SRM 1544], are in progress.

Measurement quality assurance services are provided to support major efforts within other Federal Agencies including the EPA, DoD, National Cancer Institute (NCI), National Oceanic and Atmospheric Administration (NOAA), National Institute on Drug Abuse (NIDA), and Minerals Management Service (MMS). The NCI program serves approximately 70 laboratories world-wide involved in studies to determine the cancer preventive benefits of dietary intakes of selected micronutrients to high risk human populations. During the past year, Ms. Jeanice Brown-Thomas and Dr. Katherine Sharpless were cited by the NIST Office of Measurement Services for their outstanding measurement method research, SRM development, and quality assurance activities in support of this network of laboratories. We are serving as the analytical reference laboratory for over 40 laboratories involved with the measurement of PAHs, PCBs, and chlorinated pesticides in marine sediments and tissues as part of NOAA and EPA marine monitoring programs. We are also interacting with eight laboratories involved in the measurement of heavy metals, pesticides, and PAHs in soil, water, food, and indoor/outdoor air samples being taken in the state of Arizona and EPA Region

V to provide critical information about the magnitude, extent, and cause of human exposure to important pollutants for the EPA National Human Exposure Assessment Study (NHEXAS). NHEXAS is designed to provide the information needed by citizens, public health officials, legislators, and regulators for making informed decisions about environmental health risks. In addition, we have worked with NIDA on the development of methods and standards for the analysis of drugs-of-abuse in hair, and with DoD on the development of trace organic analysis methodology for microsamples and chemical measurement protocols to be used during industrial onsite inspections for compliance with the pending Chemical Warfare Agent Treaty.

Gas Metrology and Classical Methods

Research activities within this group are focused on the development and application of methods in gas metrology and classical analytical chemistry. Laboratory research activities are focused on classical wet chemical methods, coulometry, ion chromatography, gravimetry, titrimetry, and maintenance of the theoretical infrastructure for pH and conductivity measurements.

We are assisting the U.S. automobile industry in developing and evaluating new analytical measurement tools and standards needed to address compliance issues associated with the Clean Air Act of 1990. We are developing an infrared-based sensing device and working with the NIST Physics Laboratory to evaluate a new microwave device for detection of oxygenated hydrocarbons in automobile exhaust. New standards projects in this area include: a 0.25 ppm **Propane in Air** SRM [SRM 2764] to extend the NIST series of standards to the range needed for measuring hydrocarbon exhaust emissions from next generation vehicles; a complex low-level volatile organic compounds mixture, **Ambient Non-Methane Organics in Nitrogen** [SRM 1800] to evaluate various new technologies for measuring non-methane organic compounds; catalytic conversion technology for on-demand generation of formaldehyde in air mixtures from methanol in air standards; a suite of oxygenated gasoline standards [SRMs 2286-2293] required by Federal and California regulations to document mass percent of oxygen in all commercial gasolines; and a synthetic gasoline material being certified for benzene, total aromatic content, total oxygen content, total olefin content, and sulfur, providing NIST traceability for the new reformulated gasolines.

In addition to the new standards activities mentioned above, 17 gas SRMs and 64 spectrometric solution standards were renewed during the past year. While these standards are critically needed, their continuous production consumes considerable fiscal and human resources and limits our ability to address new standards needs. Dr. Franklin Guenther and Mr. William Dorko were awarded the 1995 Edward Bennett Rosa Award for their conceptualization and implementation of the **N**IST **T**raceable **R**eference **M**aterials Program to address this problem. An NTRM is a reference material produced and sold by a commercial supplier with a well-defined traceability linkage to existing NIST standards. This linkage is established via criteria and protocols defined by NIST that are tailored to meet the needs of the metrological community to be served. Reference materials producers adhering to these requirements will be allowed to use the NIST "NTRM" trademark.

The gas NTRM program was conceptualized in 1992 in partnership with EPA and specialty gas companies as a means for providing end-users with the wide variety of certified gas standards needed to implement the "Emissions Trading" provision of the 1990 Clean Air Act. Gas NTRMs are produced and distributed by specialty gas companies with NIST oversight of the production and involvement in the analysis, and can be developed for any pollutant, concentration, and balance gas combination for which an NIST primary standard suite currently exists. Certified concentration values are assigned by NIST according to a published protocol. In FY95, six commercial vendors produced over 1300 NTRMs (70 batches). Since no NIST procurement of materials is involved, NTRM production and certification requires about a quarter of the time for production and certification of a corresponding SRM. According to Stephen Miller, Technical Director, Scott Specialty Gases, the NTRM program has served as an excellent vehicle for production of the high quality standards--of known pedigree--required by both industry and the regulatory

community in the implementation of Title IV (SO_2 emissions trading) of the 1990 Clean Air Act. Plans are being put in place to extend the Gas NTRM model for the commercial production of a wide range of reference materials with well-defined NIST traceability to other sectors of the commercial reference materials community with initial emphasis on spectrometric solutions.

Structured intercomparison programs with other National Metrology Laboratories continues to be our basis for formally establishing equivalence of primary methods and standards important for world trade and commerce. During FY95, the "Declaration of Equivalence" for primary gas standards between NIST and the Netherlands Measurements Institute (representing the European Union) was expanded to include CO, CO_2, C_3H_8, and C_2H_5OH in nitrogen over wide concentration ranges. Talks were initiated concerning new intercomparisons between NIST and the European Union in the areas of conductance and pH.

In addition, we were involved in the determination of NO/NO_2 kinetics for child inhalation research and conducted chemical assays to determine the exact formula stoichiometry of Mo_5Si_3 and Mo_3Si. The NO/NO_2 kinetics investigation was done in collaboration with the National Institute for Child Health and Development to assist pediatric researchers - who are clinically evaluating inhaled nitric oxide (NO) therapy - understand the kinetics of nitrogen dioxide (NO_2) formation under clinical conditions. Exact formula stoichiometry is a critical part of determining the thermodynamic properties of Mo_5Si_3 and Mo_3Si important in the aircraft and other high technology industries. More information concerning these two activities can be found later in the technical highlights section.

Chemical Sensing and Automation Technology

Activities in this group are directed toward the development and application of new chemical sensing technologies, new sample preparation techniques, and laboratory automation for chemical analysis. These activities are precursors to the development of new techniques and technologies that benefit U.S. industry, scientific organizations, and other government agencies and that provide foundations for standards development activities which benefit producers and consumers world-wide.

Fourier transform-near infrared/fourier transform Raman spectroscopy was explored for through-ampoule determination of oxygenates in gasoline SRMs. This non-destructive technique can be used to monitor individually the quality of each vial of an SRM material that is certified "officially" by batch. Studies of electrooptic sensors with optically transparent thin film electrodes were undertaken to see if an electrochemical reaction could be promoted on the surface of a planar optical waveguide. A method for embossing grating couplers directly onto planar waveguides has been developed and a patent application has been submitted. Future work will concentrate on specialized gratings for white light applications.

A patent was awarded during the past year for the Flow-Injection ImmunoAssay (FIIA) technology developed by Ms. Laurie Brown and Dr. Anne Plant (Biotechnology Division). Recently a new, simpler FIIA protocol was developed for measuring therapeutic drugs, and a new technique using FIIA with LC columns for separation was developed which dramatically speeds up the analysis (~2 minute per assay) and reproducibility of the method (<1% error). Studies were initiated on micro-FIIA technology to develop a "FIIA-on-a-chip" device using semiconductor processing technology to fabricate the device on a glass substrate. The hope is that such devices can be made inexpensively enough to be used only once, eliminating the need to clean the device after each use.

Supercritical fluid extraction was coupled with radioimmunoassay detection to provide a simple, automatable technique to determine drugs-of-abuse (cocaine) and their metabolites in hair samples with great sensitivity and specificity.

Efforts aimed at developing standards for laboratory automation systems integration in conjunction with the ten-member Consortium on Automated Analytical Laboratory Systems (CAALS) were carried out using our new Laboratory Automaton System Testbed (LAST) consisting of an automated SFE, automated "Prep Station," gas chromatograph, and laboratory robot. Work was begun to implement

the CAALS-I communication protocol and a generic Windows-based CAALS-I kernel for the components of the LAST. The LAST was equipped with a multi-camera machine vision system to begin a systematic examination of error and exception detection and handling in automated systems. The initial set of requirements for a device capability dataset, a database which describes what an instrument can do in computer usable (not just readable) terms, was completed, and a prototype is currently being built.

Nuclear Analytical Methods

Research activities in this group are focused on the science that underpins the identification and quantitation of chemical species by nuclear analytical techniques. Laboratory research activities are ongoing in neutron focusing technology and the full suite of neutron activation analysis methods (NAA), prompt gamma activation analysis (PGAA), and neutron depth profiling (NDP). The measurement capabilities that reside in this group provide an excellent complement to those in the Spectrochemical Methods Group in that many do not require sample dissolution.

NAA is a powerful reference technique in use at NIST for many years, new developments continue to provide improvements in detection sensitivities, elemental specificity, precision, and overall accuracy.

During the reactor shutdown, a new pneumatic tube system has been designed and installed into the NIST nuclear reactor. This fast pneumatic tube will propel the sample out of the irradiation facility and into the counting location in 0.5 second or less, and measure irradiation and decay times to within 0.01 second, allowing the determination of nuclides with half-lives as low as one second. This facility will provide NIST with the capability for accurately determining fluorine through ^{20}F ($t_{1/2}$=11.00 s) at low levels. Another improvement will be to the determination of selenium through ^{77m}Se ($t_{1/2}$=17.4 s), along with the possibility of measuring lead (at elevated levels) using ^{207m}Pb ($t_{1/2}$=0.8 s). The irradiation facility will have a highly thermalized neutron spectrum like our other, slower pneumatic tube systems. A future modification is planned to provide a second position located in an area with a highly epithermal component to the neutron spectrum. This second location will offer the possibility of substantially improving sensitivity for the determination of iodine and other elements with high resonance integrals. The entire irradiation terminal (constructed by an outside contractor) was inserted into the reactor in September, 1995. After installation of the redesigned shielding, the complete computer-controlled irradiation system should become operational about March, 1996.

Pioneering research is conducted in this Group on the use of neutron beams as analytical probes with both PGAA and NDP. PGAA measures the total amount of an analyte present throughout a sample by the analysis of the prompt gamma-rays emitted immediately following neutron capture. NDP, on the other hand, determines concentrations of several important elements (isotopes) as a function of depth within the first few micrometers of a surface by energy analysis of the prompt charged-particles emitted during neutron bombardment. NDP continues to make important contributions in the characterization of advanced materials, especially semiconductors. The non-destructive nature of NDP permits the identical sample to be characterized both before and after various physical/chemical processes, such as annealing, are applied. This allows the industry to accurately determine the effects of such processes. In addition, NDP provides reliable depth and concentration information when profiling through an interface layer, unlike Secondary Ion Mass Spectrometry (SIMS), which is often used by this industry. In fact, NDP has been used to certify the boron concentration in SRM 2137, **Boron in Silicon** as well as to check the calibration of various industrial SIMS instruments.

During the reactor shutdown, considerable effort was directed toward the upgrade of the PGAA and the NDP instruments in the Cold Neutron Research Facility. The modifications made to these instruments, and to the CNRF, are expected to yield improvement in signal-to-noise ratio, detection limits, and analytical accuracy, as well as to facilitate sample mounting and general operation of the instruments. The new cold source operates at 20 K (10 degrees colder than the D_2O source), yielding both a higher neutron flux at the analytical instruments, and larger neutron capture cross

sections for most elements. Preliminary measurements indicate a factor of about 5 improvement in neutron capture rate over that obtained with the old cold source. Additional modifications to the PGAA instrument should lead to improved measurement accuracy as well as to make the instrument more user friendly.

Our division is playing a key role in a new technology that can focus cold neutrons. During the past year, *Research and Development Magazine* selected this "Glass Polycapillary Neutron Focusing Optic" co-developed by Drs. David Mildner and Heather Chen, (Analytical Chemistry Division); X-Ray Optical Systems, Inc., Albany, New York; and the State University of New York at Albany, to be recognized as one of the hundred most technologically significant new products of 1995. The neutron focusing optic has been used at NIST to compress a rectangular neutron beam with a 45 mm x 50 mm cross section to a spherical beam with a 0.53 mm diameter. This compression in size produces a neutron current density 80 times higher than obtained at the exit of a neutron guide without the neutron focusing optic.

We continue our long-range plan to explore and develop the analytical applications of the focused neutron beam. Such beams will greatly enhance the capabilities of both PGAA and NDP. A high intensity beam on a small sample area will be useful for improving the detection limits of individual elements in small samples, as well as for providing compositional mapping information. For example, a beam of neutrons focused to a small spot size would allow three-dimensional mapping of semiconductor materials by NDP. Since dopant uniformity is often an important parameter in the performance of semiconductor devices, such information would be extremely valuable for this industry.

<u>*New Directions*</u>

All Division research and service projects are reviewed on an annual basis for quality and match to mission and customer needs. Projects that are not progressing or have successfully come to completion are terminated in favor of new ones. The general focus of the research and measurement service activities within the Division will not change very much in the coming year except in our Chemical Sensing and Automation Program, where our attention to measurement and standards needs in the area of process analytical chemistry will increase. This increased emphasis on real-time measurement and standards issues is reflected in the following list of new projects that will be initiated in FY96:

- Sample Modulation in Atomic Spectrometry
- On-Line Coulometry for Process Applications
- Packed Column Electrokinetic Capillary Chromatography
- Compositional Mapping by Neutron Depth Profiling Using a Neutron Probe from a Monolithic Lens
- Mass Spectrometry as a Tool for Characterization and Standardization of Clinical Immunoassays
- Quantitative Gas-Phase Database for FTIR Remote Sensing Applications
- Combined NIR/Raman Instrumentation for Process Analytical Measurements
- Low-Level Light Standards for Chemiluminescence and Other Photon Counting Detectors
- As and Hg Speciation in Marine SRMs
- Methods and Standards for Oxygenated Hydrocarbons in Automobile Exhaust

The Division receives approximately $2.5M annually for the development of SRMs. The vast majority (~93%) of these funds have, in the past, been used for renewals urgently requested by customers. The NTRM program described previously is beginning to provide some relief in this regard. In FY96, efforts will begin for development of the following new SRMs:

- Reformulated Gasoline (*Oxygenates, organic and total sulfur, and aromatics to be certified).*
- Hydrogen on Titanium (*Brittleness of aircraft turbine blades related to H_2 concentration).*
- Zeolite Catalysts (*Na, Si, Al, Fe, and trace metals to be certified).*

- Aircraft Alloys (*P and S to be certified; these elements related to materials failure).*
- Canned Meat for Nutrition Labeling (*Cholesterol, fatty acids, and minerals to be certified).*

The information that has been provided represents a broad range of research and service activities within the general area of chemical measurement science. This overview plus the Selected Technical Reports and Outputs and Interactions sections that follow provide additional details concerning our work and reflects the high quality of our staff. This information also shows how our efforts impact U.S. industry's productivity, competitiveness, and equity in trade, and supports environmental quality, public health, and safety.

B. Selected Technical Reports

1. *Accurate Wavelength Calibration using UV/Vis-Fourier Transform Spectroscopy*

M.L. Salit, J.C. Travis, and M.R. Winchester

Objective: This work is being pursued to accurately measure atomic emission wavelengths in the Inductively-Coupled Plasma source using UV/Vis-Fourier Transform Spectroscopy (FTS). This source is widely used for chemical metrology, and its accurate characterization will enhance the robustness of chemical measurements.

Problem: (1) Wavelength errors in FTS arise from geometric illumination effects at the entrance aperture, and can be limited to a couple of parts in 10^7. Use of an intrinsic wavelength standard can improve this, if the calibration standards can be trusted under the operating conditions where they are being observed. An approach was required to utilize external standards without compromising the accuracy of the calibration. (2) Anomalous wavelength calibration results triggered research into FTS calibration problems, initially targeted at uncovering biases in the FTS measurement. Initially, calibration factors from widely used Ar wavelength standards were observed to have a systematic bias (slope) with photon energy. Examination of calibration factors from ^{198}Hg wavelength standards (several of which are international secondary standards of length) revealed a similar trend.

Approach: A unique optical coupling scheme was developed which enables unprecedented wavelength accuracy in FTS. This coupling scheme allows us to overcome the uncertainty associated with the illumination effects and to achieve accuracy limited only by the precision of the measurement of the calibration standards (several parts in 10^9), and is applicable to any wavelength region. Utilizing an integrating sphere to mix the light from a clock-based laser frequency standard with the light from the source under investigation, wavelength accuracy limited by the precision of the measurement should be attainable. The integrating sphere significantly attenuates the light, limiting the high accuracy measurements to the brightest lines.

To resolve the source of the anomalous calibration results, potential contributions to the bias arising from operating parameters (pressure and temperature) for the standard sources were investigated, and systematically ruled out. Parameters of the spectroscopy were characterized, including entrance illumination, aperture, line shape symmetry, and resolution, and were also systematically ruled out. Finally, the internal consistency of energy levels derived from the FTS line positions was compared to the internal consistency of the original standards. Further experiments were performed to characterize the slope, using a stabilized CW laser and its harmonic (with the collaboration of C. Sansonetti and D. Veza of the Physics Laboratory). To validate the wavelength scale in FTS, the frequencies observed for these laser lines had to be in a ratio of exactly 2:1.

Results and Future Plans: Feasibility of the integrating sphere was demonstrated for both a ^{198}Hg wavelength standard and the ICP emission source, with adequate signal-to-noise to make wavelength measurements with uncertainties of less than 1 part in 10^8. Internal consistency of the FTS ^{198}Hg results were found to be superior to the results from which the original wavelength standards were derived. Evaluation of the FTS wavelength scale with the laser and its harmonic verified that the scale is valid to at least the part in 10^8 level. New ^{198}Hg wavelengths have been measured, using the frequency stabilized laser locked to a clock-based standard. Small deviations from an exact ratio of 2 in the laser experiment, and the trends of this ratio with time are being evaluated. Line shape asymmetry in the FTS instrument function is being examined for possible contributions to uncertainty. New ^{198}Hg wavelength standards will be measured in a series of lamps to produce new secondary standards of length.

Publications:

Salit, M., Travis, J., and Winchester, M., "***Practical Wavelength Calibration Considerations for UV-Visible FTS.***" Applied Optics (in press).

2. *Optically-induced Analytical Error in Glow Discharge Optical Emission Spectrometry*

M.R. Winchester

Objective: To improve the reliability of glow discharge optical emission spectrometry (GDOES) for chemical analysis.

Problem: GDOES has been used for many years for the elemental analysis of materials directly in the solid state. Although the technique has been traditionally applied to the analysis of electrically conductive materials such as metals and alloys, its applicability has recently been extended to electrically nonconductive materials such as ceramics, glasses and polymers, as well as to the depth-resolved analysis of thin films.

Despite the relatively widespread applicability and use of the technique, the optical systems used to measure optical emission from the glow discharge device have in some respects remained in a state of developmental infancy. Specifically, the optics used to transfer emission from the device to the spectrometer usually consists of only a single lens, which images the discharge onto the entrance slit. The suitability of this simple-minded approach for application in analytical GDOES has met with little if any scrutiny.

In a recent paper, Hoffmann and Ehrlich [*Spectrochim. Acta* **50B**, 607 (1995)] reported that sample material did not mix thoroughly in the gas phase in their glow discharge device. As they pointed out, this suggests that the use of a single lens to image the discharge onto the entrance slit may induce analytical error when the sample is chemically heterogeneous.

Approach: In order to investigate the existence and severity of optically-induced error of the type mentioned above, the behavior of GDOES with samples known to be chemically heterogeneous was evaluated. Two samples were used. The first was a synthetic sample consisting of a brass surface with a 1 mm diameter implanted steel plug. Since this sample is not realistic in terms of its severity of heterogeneity, a second sample was also employed. This sample was a brass disc that had been rejected previously as a standard reference material, owing to a small Pb heterogeneity.

Results and Future Plans: Studies with both samples indicated the presence of optically-induced analytical error. The error demonstrated for the synthetic sample was about 35%, indicating that the error can be large. In two trials, the error associated with the more realistic sample was between 1% and 2%. Though relatively small, this level of error is of concern in quantitative GDOES analyses.

Elimination of the optically-induced error was attempted with the use of an alternative optical transfer method. This method, suggested in the previous publication, utilizes two lenses to transfer emission from the discharge device to the entrance slit. The alternative approach successfully eliminated the error for both the synthetic and "real-world" samples. These results suggest that the two-lens system should be routinely employed in analytical GDOES.

During FY96, the use of the two-lens method in GDOES will be characterized in terms of analytical figures of merit. These figures of merit will include signal-to-noise ratios, signal-to-background ratios, sensitivities, and limits of detection for various elements and samples.

Publications:

Winchester, M.R., **"Optically-induced Analytical Error in Glow Discharge Optical Emission,"** Applied Spectroscopy 50, 245-251 (1996).

3. *Isotope Dilution Mass Spectrometric Analysis Using Continuous Flow Microwave Sample Digestion*

E.S. Beary, P.J. Paulsen, and J.D. Fassett

Objective: To evaluate the performance of a commercial continuous flow microwave device for use as an alternative to conventional dissolution procedures for isotope dilution mass spectrometric analyses.

Problem: Sample preparation is often the most labor-intensive and time-consuming part of chemical analysis procedures. This commercial device could simplify chemical procedures, and minimize potential errors due to contamination, incomplete digestion, or loss of volatile analytes.

Approach: Isotope dilution inductively coupled plasma mass spectrometry (ID-ICPMS) with continuous flow microwave dissolution was used to determine lead in a broad range of environmental and clinical SRMs: dust, fuel, air filters, leaves, paint, sludge, and urine. These materials have been previously certified for lead using IDMS and traditional sample preparation procedures; therefore, the results were directly comparable. Homogeneous mixing of the sample and the enriched isotope used as an internal standard is a critical aspect of accurate ID-ICPMS. Under such conditions, accuracy and precision of <0.2% relative has been demonstrated. Traditionally, equilibration of sample and spike is accomplished during a total sample dissolution, or wet digestion. With the continuous flow system, a fraction (4-20%) of the slurried sample is introduced using an autosampler. The subsample is transported into the microwave coil via a carrier stream of high purity water. Therefore, accuracy is dependent upon isotopic mixing during the automated sampling, and prior to dissolution.

Results and Future Plans: No significant differences between batch and continuous flow techniques were evident with respect to both accuracy and precision. In addition, subsamples taken with a 2 mL sample loop behaved identically with those taken with the 10 mL sample loop, despite the large relative difference in "effective" sample size. The highly successful application of this procedure to lead analyses may be partially due to the fact that lead is readily solubilized in certain acid mixtures. Future plans include the study of other elements, such as Ti and Sn which are not so readily solubilized.

4. *Development of a Mass Spectrometric Reference Method for Human Serum Albumin*

D.M. Bunk and M.J. Welch

Objective: To develop a reference method for the determination of albumin in human serum.

Problem: The certification of clinical protein reference materials is frequently done with methods which only indirectly measure the protein of interest. Indirect methods such as immunoassay are prone to errors from matrix interferences, which can result in substantial variability in assay results from method to method.

Approach: Mass spectrometry measures the protein directly, providing high sensitivity and selectivity through relative molecular mass information. Electrospray ionization mass spectrometry (ESI-MS) has been extensively used for the qualitative analysis of proteins but not for protein quantitation. Building on model studies of protein quantitation done in FY94 with ESI-MS, the quantitation of albumin in human serum was performed by coupling capillary reversed-phase liquid chromatography with ESI-MS. With a separation technique prior to mass analysis, this method requires no sample treatment other than dilution with an appropriate internal standard. A biotinylated albumin was prepared to be used as an internal standard for the determination.

Results and Future Plans: A preliminary determination of albumin in fresh-frozen serum was performed, yielding a result that was within the expected range of serum albumin concentrations, with a relative standard deviation of approximately 3% for replicate analysis. Less than 1 µL of serum was needed for this determination.

Upon examination by LC/ESI-MS of freeze-dried and fresh-frozen serum, a substantial difference was observed in the mass distributions of their albumin. The albumin in the freeze-dried serum has a slightly larger mass and substantially greater mass heterogeneity than that in fresh-frozen serum (see Figure 1). The mass distribution of the albumin from fresh-frozen serum was identical to that of pure albumin standard.

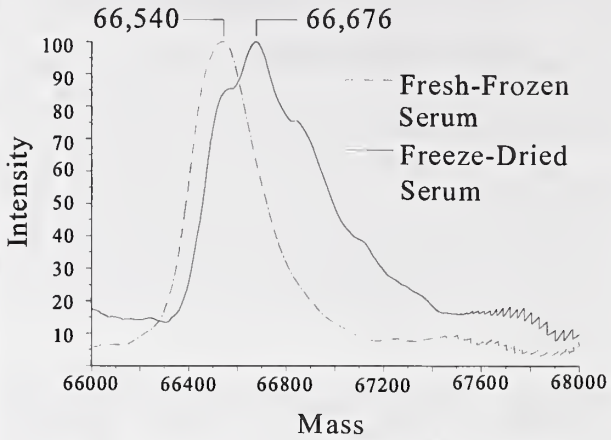


Figure 1. Mass distribution of albumin in fresh-frozen and freeze-dried serum.

Structural analysis of the albumin in freeze-dried serum indicated an increased level of non-enzymatic glycoslyation, most likely the result of the reaction of serum glucose with the amino groups of albumin during the freeze-drying process.

The determination of albumin in human serum is intended to be a test case for the analysis of other clinically relevant serum proteins. Using many of the methodologies developed for the analysis of albumin, additional work is in progress for the determination of glycohemoglobin in blood, a very important clinical marker for diabetes. This measurement technology will also be used for the characterization of the monoclonal antibodies used in the immunoassay of creatine kinase MB, a marker for acute myocardial infarction.

During FY96, a more extensive study will be done comparing the mass spectrometric method with the conventional spectroscopic methods used for clinical albumin determination. The goal of this study will be an assessment of the accuracy of the mass spectrometric method relative to the methods that are in current use.

5. *Development, Validation, and Application of a Method for the Measurement of Methylmercury in Marine Samples Based on Gas Chromatography with Atomic Emission Detection (GC-AED)*

M.K. Behlke, M.M. Schantz, and S.A. Wise

Objective: To develop a method for determination of methylmercury in marine samples and apply the method to value-assign NIST SRMs.

Problem: Many damaging chemicals have been introduced into the marine environment during the last few decades. Organo-mercurials are among the most toxic of these contaminants due to their tendency to accumulate in biological tissues. A variety of analytical methods have been developed for the speciation of mercury compounds in marine materials. However, most of these methods are time consuming and inherently problematic. Furthermore, only a limited number of reference materials (RMs) for methylmercury are available and none are currently available from NIST. Different matrix types value-assigned for a wider range of methylmercury concentrations are desperately needed for quality assurance and method development in this field.

Approach: A new method has been developed for the extraction, separation, and detection of methyl- and ethylmercury chloride in fish and marine mammal tissues and human hair. Samples are extracted with organic solvent under acidic conditions to separate the analyte from the sample matrix. Interfering sulfur-containing species are removed during extraction with copper powder. Lipids and pigments are removed from the extract by preparative gel permeation chromatography. Analytes are separated by gas chromatography and detected at 253.7 nm with an atomic emission detector (AED). The chromatographic separation and atomic emission detection were optimized for a variety of parameters.

Results and Future Plans: An absolute detection limit of 0.8 pg methylmercury chloride (as Hg), which was achieved using the optimized GC-AED conditions, is a 100-fold improvement over previously reported comparable methods. The entire extraction, cleanup, and detection procedure was validated using four Certified Reference Materials from the National Research Council (NRC) Canada and the International Atomic Energy Agency (IAEA). Thirteen reference materials including nine NIST SRMs were screened for methylmercury content to identify candidate materials for value-assignment. Replicate analyses of each material produced relative standard deviations below 10% for most materials except where inhomogeneity is suspected. Additional measurements were made on SRM 1974a, Organics in Mussel Tissue and SRM 2974, Organics in Freeze-dried Mussel Tissue, to provide the first NIST assigned methylmercury values for NIST SRMs. Measurements were also made on two candidate human hair reference materials from the IAEA as part of an inter-laboratory comparison exercise with excellent agreement between the NIST method values and the overall exercise means. Methylmercury measurements were performed on beluga whale liver samples from the Alaskan Marine Mammal Tissue Archival Project (AMMTAP). Agreement was observed between results obtained using the new NIST method and previous measurements made by the Institute of Applied Physical Chemistry, Research Center Jülich (Germany) on sub-samples of identical specimens. Future plans include using the GC-AED method to measure methylmercury in additional AMMTAP samples, including beluga whale kidney, blubber, and skin samples to investigate the distribution of methylmercury in various tissues from the same animals.

Publications:

Behlke, M.K., Uden, P.C., and Schantz, M.M., **"Investigations of Sulfur Interferences in the Extraction of Alkylmercury Halides from Marine Tissues,"** Analytical Proceedings (in press).

Behlke, M.K., Uden, P.C., Schantz, and Wise, S.A., **"Development, Validation, and Application of a Method for Organomercury Speciation in Biological Marine Materials by Gas Chromatography-Atomic Emission Detection (GC-AED),"** Analytical Chemistry (in press).

6. *Investigation of Supercritical Fluid Chromatography (SFC) for the Separation of Chiral Compounds of Pharmaceutical and Agricultural Interest*

K.L. Williams, L.C. Sander, and S.A. Wise

Objective: To investigate the use of supercritical fluid chromatography for the separation of enantiomers of pharmaceutical and agricultural interest.

Problem: Synthetic chiral pharmaceutical and agricultural chemicals are frequently marketed as an equimolar mixture of enantiomers, known as a racemate. Despite the fact that the enantiomers are mirror images of each other, they do not always display identical behavior in living systems. In fact, one enantiomer of the racemate may exhibit therapeutic activity while the other produces undesirable side effects. Identification of differences in enantiomer activity and/or toxicity has been hampered by the difficulty associated with separating the enantiomers of the racemate. However, evaluation of the efficacy of the individual enantiomers is desirable for the development of safe and effective chiral drugs and pesticides.

Approach: The most prevalent strategy for enantiomer separations has been to use chiral stationary phases (CSPs) for liquid chromatography (LC). Problems associated with this approach include poor peak resolution, long analysis times, and instability of the CSP under some mobile phase conditions. Recently, supercritical fluid chromatography (SFC) has been proposed as an alternative to LC for enantiomer separations. Potential advantages of SFC include reduced analysis time, improved peak resolution, and simplified method development when compared to LC techniques.

Results and Future Plans: Direct comparisons of LC and SFC were performed using several commercially available CSPs. Chromatographic analyses in SFC were performed using carbon dioxide as the principal eluent. Alcohol modifiers were added to the carbon dioxide to elute polar compounds. Enantio-separations of numerous pharmaceutical and agricultural racemates were used to assess the applicability of SFC for chiral separations.

The mobile phase is often an integral part of the success or failure of chiral separations in LC. Some CSPs can be utilized under both normal and reversed phase conditions, making mobile phase selection even more complex. In SFC, separations analogous to both normal and reversed-phase LC separations were achieved with a carbon dioxide-alcohol eluent. Therefore, optimization of the enantiomeric separation was simplified dramatically in SFC. The higher flow rates used in SFC also reduced the time required for each analysis. As a result, method development time was often reduced to just a few minutes in SFC.

For the compounds and CSPs studied, SFC generally provided better peak resolution than LC. Peak resolution is an important parameter for the accurate measurement of small amounts of one enantiomer in the presence of a large excess of the other enantiomer. Improved peak resolution also minimizes interference from impurities or other constituents present in the sample. In some instances, separations could be achieved in SFC that were not possible on the same CSP in LC. Hence, SFC can expand the range of racemates resolved on a particular CSP, and reduce the number of expensive CSPs that must be evaluated during method development.

Although SFC has tremendous potential, the use of SFC for chiral separations is still relatively new. Future studies will involve identification of additional applications of SFC and will focus on areas where SFC is likely to provide improvements over other techniques.

Publications:

Williams, K.L., Sander, L.C., and Wise, S.A., **"Use of a Naphthyl-ethylcarbamoylated-β-Cyclodextrin Chiral Stationary Phase for the Separation of Drug Enantiomers and Related Compounds by Sub- and Supercritical Fluid Chromatography,"** Chirality (in press).

7. *Development and Evaluation of Liquid Chromatography Stationary Phase Tailored for Carotenoid Separations*

L.C. Sander

Objective: To develop a new liquid chromatography stationary phase optimized for the separation of carotenoid isomers.

Problem: Carotenoids constitute a class of compounds that occur naturally in fruits and vegetables and are generally present in mixtures of considerable complexity. Existing liquid chromatographic columns are unable to resolve many carotenoid isomers. Because carotenoids are thought to be a factor in the prevention of disease, separation and measurement of the individual isomers is of considerable importance.

Approach: To a large extent, column selectivity in liquid chromatography is controlled by bonded phase morphology, particularly for solutes with similar size and shape (e.g., isomers). The selection of suitable substrate properties (particle size, pore size, and surface area) and surface modification procedures (ligand and phase type) permits wide variations to be created in the retention properties of the resulting bonded stationary phase. An understanding of the processes that govern retention permits prudent selection of these variables for the production of phases tailored for a specific application.

Results and Future Plans: Several approaches were combined in the development of the tailored "carotenoid column." The retention behavior of selected carotenoid probes was studied for monomeric and polymeric C_{18} columns. Polar carotenoids (xanthophylls) were best separated with monomeric C_{18} columns, whereas polymeric C_{18} columns were best suited for the separation of nonpolar geometric carotenoid isomers. It was further observed that better separation of isomers was possible with long chain length stationary phases, and that "endcapping" (a common process to reduce stationary phase silanol activity) was detrimental to the separation of xanthophylls.

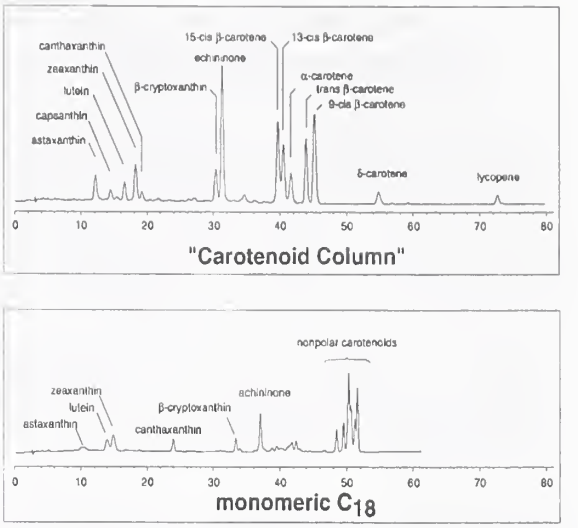


Figure 1. Column comparison.

To achieve these combined qualities in a stationary phase, the following "recipe" was used. A C_{30} stationary phase was synthesized using polymeric surface modification chemistry on a 200 Å, 200 m^2/g silica substrate, without subsequent endcapping. Significantly improved separations of polar and nonpolar carotenoid isomers have been demonstrated with this engineered column (Figure 1).

The development of a carotenoid column represents a practical application of years of basic research regarding chromatographic retention processes. We have published this information in the open literature and have worked with a manufacturer of chromatographic columns (YMC, Inc., Wilmington, NC) to make this technology available to the practicing analyst. Columns based on this technology are currently available and reports are appearing in the literature indicating use by the carotenoid measurement community. This program is an example of how basic NIST research has been applied to solve problems of broad health and nutritional concerns. Future work is planned to develop related stationary phases based on very long chain length ligands (ca. C_{36}-C_{42}).

Publications:

Sander, L.C., Sharpless, K.E., Craft, N.E., and Wise S.A., **"Development of Engineered Stationary Phases for the Separation of Carotenoid Isomers,"** Analytical Chemistry 66, 1667-1674 (1994).

8. *NO/NO_2 Kinetics for Child Inhalation Therapy Research*

W.J. Thorn III, P.M. Chu, and R.L. Sams, L. Wright (National Institute of Child Health and Development); O. Rivera (Children's National Medical Center); G. Sokol (Indiana Univ. Medical Center) and K. Van Meuers (Stanford Univ.)

Objective: To assist pediatric researchers who are clinically evaluating inhaled nitric oxide (NO) therapy understand the kinetics of nitrogen dioxide (NO_2) formation under clinical conditions.

Problem: Pediatric researchers are working under National Institute of Child Health and Development and Food and Drug Administration guidelines to evaluate the therapeutic value of inhaled NO in newborn patients. Dilute concentrations (< 100 µmol/mol) of NO have shown dramatic results as a pulmonary vasodilator in some newborn patients when inhaled with oxygen via a ventilator. However, once the NO is mixed with oxygen spontaneous formation of NO_2 occurs. Nitrogen dioxide can carry pulmonary edema and other problems in the respiratory system, especially at concentrations above 5 µmol/mol.

The kinetics of NO_2 formation have been studied by atmospheric chemists due to its importance in smog formation. NIST periodically performs a critical review of reported kinetic data, the most recent in 1992. However, some of the currently measured NO_2 concentrations reported by clinical researchers seem to be in conflict with the accepted kinetic model. NIST was asked to independently evaluate these kinetics under clinical conditions, defined as 90% oxygen at ambient conditions.

Approach: NIST SRM 2735 containing 800 µmol/mol NO was dynamically diluted 1:9 with oxygen at total flowrates of 3 L/min to 10 L/min. A Sechrist ventilator was modified with mass flow controllers to achieve short dwell times, while a specially designed mixing volume was used to achieve longer dwell times. A chemiluminescent monitor was calibrated with NIST SRM 1683b (48 µmol/mol NO) and SRM 1684b (96 µmol/mol NO) and then used to monitor NO levels reaching the patient. The amount of NO_2 reaching the patient was measured using NIST's tunable diode laser absorption spectrometer (TDLAS) which can measure NO_2 with a sensitivity of 20 nmol/mol independent of the oxygen concentration. The performance of chemiluminescent and electrochemical instruments used in clinical studies was also evaluated under these conditions.

Results and Future Work: NO_2 formation was measured by TDLAS as a function of system dwell time, the time which elapses from initial mixing of NO with the oxygen to the mixture reaching the patient (TDLAS cell). Data was taken for dwell times from 1 s to 13 s. The rate of NO_2 formation under these conditions were measured to be (0.144 ± 0.006) µmol/mol^{-1}s^{-1} per second of dwell time, which is in good agreement with the accepted kinetic model and rate constant. Since clinical dwell times are normally less than one second, no measurable NO_2 should form before reaching the patient.

NO_2 electrochemical sensors did not work well in the 90% to 100 % oxygen matrix. They indicated NO_2 concentrations orders of magnitude higher than actually present. Chemiluminescent based instruments registered negative values for NO_2 under these conditions. These observations may explain the previously reported results which deviated from the accepted kinetic model.

In order to have a NIST-verified NO standard for clinical researchers to calibrate their instrumentation, we worked with a commercial specialty gas company to value assign an 85 µmol/mol NO standard mixture. Furthermore, quality assurance procedures were jointly developed to minimize NO_2 contamination in source gases used by researchers during inhaled NO trials. A paper is being prepared which will detail this work for clinical researchers. No further efforts are planned at this time.

9. *Development of New Technology for On-Demand Generation of Formaldehyde in Air Standards*

P.M. Chu, R.L Sams, and W.J. Thorn III

Objective: To develop a procedure for on-demand generation of a formaldehyde in air standard gas mixture.

Problem: The Automotive Industry/Government Emissions Research (AIGER) consortium has identified formaldehyde standards as one of its high priority items. Some of the challenges of developing this standard include the fact that formaldehyde has been observed to be difficult to stabilize in gas cylinders, and formaldehyde permeation tubes are difficult to work with.

Approach: We are developing an approach using catalytic conversion of methanol to formaldehyde. Since we already have a proven ability to produce stable methanol standards, the conversion method depends on finding a reliable catalyst with high conversion efficiency.

A tunable diode laser absorption spectrometer (TDLAS) system was used to monitor the conversion of methanol to formaldehyde. The initial work was done using several methanol sources including: 50 μmol/mol methanol in nitrogen and 45.9 μmol/mol methanol in air cylinder standards, and methanol permeation tubes. Silver wool, MoO_3, Fe_2O_3, MnO and molybdenum mesh were tested as potential catalysts. The methanol mixtures were flowed over the catalysts at different temperatures and into the long-path cell of the TDLAS system. The final concentrations of methanol, formaldehyde, methane, CO, and CO_2 were monitored by setting the TDLAS system on an appropriate transition. A Fourier transform infrared spectrometer with 0.11 cm^{-1} resolution was used to test for additional products such as acetic acid and acetaldehyde.

Results and Future Work: Previous work on this project surveyed the conversion efficiency of several different catalysts and found the highest (80-86%) conversion rate from a mixture of silver wool and MoO_3. Although there was a reasonable conversion to formaldehyde, the lack of long term reproducibility of this system was a major drawback. During FY95, we concentrated on addressing this reproducibility by: (1) developing a rack mountable prototype converter suitable for an industrial environment, providing more consistent experimental conditions, and (2) testing potential catalysts over long periods. We found that by using a molybdenum mesh catalyst the prototype provided 80% ± 4% conversion to formaldehyde over the course of several months with only CO and CO_2 as byproducts.

A large fraction of this uncertainty can be attributed to problems in delivering the methanol from cylinder standards with high precision. The delivery of the methanol through the tubing in the system proved to be difficult, probably due to "sticking" to the walls of the tubing and the cylinder valve.

In FY96 we will: (1) continue to investigate other catalysts to find the most efficient and reproducible conversion rate; (2) explore modifying the oxygen content of the balance gas, the catalyst bed length, and other alternative methods of raising the conversion rate; (3) work on improving the reproducibility of delivering methanol from the cylinder standards; (4) develop a model of the operation parameters versus efficiency to predict the formaldehyde concentration from the concentration of the methanol gas standard; and (5) build a second prototype converter for field evaluation by an AIGER participant.

10. *Chemical Assays for the Determination of the Thermodynamic Properties of Mo_5Si_3 and Mo_3Si High Temperature Materials for Supersonic Surfaces*

J.R. Moody, C.M. Beck and P.A. O'Hare

Objective: To determine the exact formula stoichiometry of Mo_3Si and Mo_5Si_3.

Problem: The interest in the thermodynamic properties of Mo_3Si and Mo_5Si_3 is due to the importance of the materials to the aircraft and other high technology industries. Although the specific enthalpies of reaction of substances like the molybdenum silicides can be measured with precision using fluorine-bomb calorimetry, the conversion of these results to a reliable standard molar enthalpy of formation requires a knowledge of the exact formula stoichiometry of the compound. This determination is done by obtaining the exact chemical composition of the same material used for the fluorine-bomb calorimetry.

Approach: The mass fraction of all impurities in the compounds was determined. The approach used was to assay the compounds for silicon and determine the mass fraction of molybdenum by difference. A high precision assay technique for silicon was developed. The procedure involves oxidizing accurately weighed samples in quartz boats inside a muffle furnace by slowly raising the temperature to 1050 °C over a period of five days. This procedure achieved two objectives. It converted the starting material to a mixture of SiO_2 and MoO_3; and, at temperatures above 650°C it caused the MoO_3 to volatilize, thus effecting the separation of the silicon and molybdenum oxides. The temperature was raised slowly to prevent the ejection of the starting material or the SiO_2 from the quartz boat by MoO_3 as it sublimed. Although SiO_2 was the predominate compound remaining after the firing in the muffle furnace, X-ray analysis revealed a small but significant mass of MoO_3 that had not volatilized. To make corrections for this, the contents of the boat were transferred to a platinum crucible and the SiO_2 was dissolved in HF and volatilized as SiF_4. The mass of the remaining MoO_3 was determined by difference and the mass fraction of SiO_2 in the original sample was calculated.

Results and Future Work: Based upon these analyses of the samples provided, the assay of nominal Mo_3Si gave a stoichiometry equivalent to $Mo_3Si_{1.000 \pm 0.003}$. The corresponding assay of nominal Mo_5Si_3 gave a stoichiometry equivalent to $Mo_5Si_{3.00 \pm 0.02}$. These stoichiometric values were subsequently used for the calculation of an accurate standard molar enthalpy of formation for these compounds. No future work is anticipated.

11. *Coupling Light into Planar Waveguide Sensors Using Embossed Grating Couplers*

S.J. Choquette and B.L. Ramos

Objective: To develop a technique for making reproducible waveguide coupler gratings that are inexpensive and easy to fabricate.

Problem: Planar waveguides are attractive tools for use in analytical chemistry and spectroscopy. Since the evanescent wave is easily accessed along the waveguide, a number of papers have addressed the use of planar waveguides for bio/chemical sensors. But, unlike optical fibers, the acceptance and use of planar waveguides has been slow due to the difficulty of coupling light into the waveguide.

Approach: Generally, light coupling with prisms is the method of choice in the laboratory because coupling efficiencies approaching the theoretical limit of 81% can be reached. However, prisms are impractical for routine use since expensive positioning equipment is required, coupled power is sensitive to environmental fluctuations, and prism coupling prohibits the fabrication of a truly planar device. Employing diffraction or reflection gratings for light coupling is a more practical alternative. Although the coupling efficiency observed with gratings is lower than that obtained using prisms, the two-dimensional nature of the guide is conserved. Furthermore, gratings are generally more robust than prisms.

Results and Future Plans: To create reproducible gratings that are inexpensive and easy to fabricate, we have developed an embossing technique using a commercial grating as the master template. By chemically modifying the surface of the commercial grating with a suitable release agent, it is possible to replicate gratings in epoxy onto a variety of waveguide types. Master gratings were silanized with a solution of (tridecafluoro-1,1,2,2,-tetra-hydrooctyl)-1,1-trichlorosilane in toluene to form the release agent. After exposing the epoxy to ultraviolet light for 1 minute, the substrate is pulled away from the release-coated master, leaving an embossed grating on the waveguide surface. When performed with care, this technique allows many replicates to be produced from a single master, thereby facilitating the fabrication of inexpensive, reproducible gratings with sufficient efficiency to be used as waveguide couplers. Furthermore, this technique is independent of waveguide type and is suitable for replicating grating profiles of different line spacing and groove shape. Because "submasters" or copies of gratings can be readily made and reused in conjunction with the new release agent, it is feasible to consider developing a custom grating for a particular application. This technology is applicable to waveguide diffractive couplers as well as any other diffractive optical elements that are currently fabricated by holographic or lithographic means. In addition, this method can be used to emboss any structure that requires a template, (e.g., channels, or steps). Future work will concentrate on the fabrication of chirped gratings for focusing and white light applications.

12. *FTIR and FT-Raman Determination of Oxygenates in Gasoline*

S.J. Choquette, D.L. Duewer, S.N. Chesler and S. Wang (Univ. of Maryland)

Objective: To develop a non-invasive method for determining mixed oxygenates in ampoules of gasoline that can be used to assure quality in NIST Standard Reference Materials (SRMs) and NIST Traceable Reference Materials (NTRMs). This technology is also being evaluated for its potential as an on-line method for monitoring refinery blending operations.

Problem: Oxygenated fuels designed to lower carbon monoxide (CO) emissions are standard gasolines blended with alcohol or ether additives. Ethanol and methyl tertiary butyl ether are the predominant oxygen additives. Tertiary amyl methyl ether and ethyl tertiary butyl ether are additional additives that are effective at reducing automotive CO emissions. NIST provides gasoline SRM and NTRM mixtures of these four oxygenates at 2.0% and 2.7% by weight in a well-characterized gasoline matrix. These materials are supplied in 20 mL sealed glass ampoules. Currently, NIST uses capillary gas chromatography with flame ionization detection (GC-FID) to certify these oxygenate mixtures. Although this technique provides excellent precision and accuracy, it cannot be used to examine each individual ampoule for homogeneity testing or quality control, since the ampoules must be opened to be sampled.

Approach: In this study, we evaluated Fourier Transform Infrared (FTIR) and Fourier Transform-Raman spectroscopic methods to identify and determine, without opening the ampoules, the oxygenate content of gasoline SRM materials. Single oxygenate blends, as well as mixtures containing two oxygenates, were investigated using both Fourier transform techniques. A multivariate statistical calibration technique (partial least squares) was applied to both the NIR and Raman data sets to obtain predictions of the weight percentages of oxygenate in the gasoline samples.

Results and Future Plans: The Fourier Transform methods are fast, simple, and accurate even though the geometrically imprecise 20 mL ampoules were used to hold the sample. The root-mean-square error of prediction for each of the four oxygenates individually was less than a mass fraction of 0.15% by nIR and about 0.4% using Raman. Similarly, prediction errors for gasoline samples containing each of the dual oxygenate mixtures were less than 0.2% by NIR and ~0.35% by Raman. To increase the robustness of the calibration, a combined model using both NIR and Raman data was devised. The absolute error of prediction using the combined NIR/Raman calibration model was less than 0.15% for all single oxygenates, while the combined model was able to predict two-component mixtures to better than a mass fraction of than ±0.5% for each oxygenate.

We are continuing this research to determine the feasibility of these techniques for the determination of more than two oxygenates per sample for NTRM and SRM quality control and homogeneity testing, and for on-line oxygenate determinations during refinery blending operations where GC-FID is too slow.

13. *Machine Vision Provides a Means for Laboratory Automation Error and Exception Handling*

***G.W. Kramer**, T.A. Staab, U. Bernhoeft, and P.J. Grandsard*

Objective: To develop a systematic approach to the means of errors and exceptions in automated analytical laboratory systems.

Problem: Management of errors and exceptions in automated laboratory systems is commonly omitted in the initial designs for laboratory automation applications. Ad hoc approaches for handling such unexpected events must be added during system implementation. This often transforms a carefully designed control system to "spaghetti code" and introduces a hodge-podge network of sensors. As a result, the system's modularity and plug-and-play features are likely to be compromised.

Approach: With the Consortium on Automated Analytical Laboratory Systems (CAALS), we are developing a module that systematically manages unexpected events. Called the error and exception management module (EMM), the module currently uses machine vision to detect abnormal events but is not limited to this type of sensor.

Results and Future Plans: The EMM operates in our Laboratory Automation System Testbed (LAST), which was created to evaluate new CAALS concepts such as the EMM. The LAST consists of a laboratory robot, an automated supercritical fluid extractor, an automated gas chromatograph (GC) with a sample preparation accessory capable of fluid and sample vial manipulations, other automated devices, and a computer-driven control system. Machine vision sensing was selected because of its universal nature. One video camera can often replace several small individual sensors while providing much additional information. So far, we have programmed the EMM to detect about forty external error/exception events on the LAST, most of which involve the sample preparation accessories for the GC.

The machine vision system uses multiple (currently four) low cost "surveillance" Charge Coupled Device (CCD) cameras to provide detailed views of portions of the system. Three of the cameras are fixed; but one camera, mounted to the robot arm, can display a variety of scenes depending on the orientation of the robot arm. Each camera feeds a PC-controlled multiplexer that outputs one of up to eight video signals to a low-cost frame grabber mounted in a Pentium-class computer that runs commercial image analysis software.

In developing the EMM, we have addressed its compliance to CAALS module specifications, the behavior requirements for the EMM as a Standard Service Module, the error and exception management functions, the EMM operation schemes, and the levels of synchronization between error/exception detection and restoration. The EMM uses databases to link detected features to events, or to link classified events to the proper restoration procedures. Our approach to error/exception handling is to reduce the idiosyncratic treatment to a systematic approach by classifying errors into types where possible. Thus far, we have developed a preliminary list of classifiers. During the upcoming year, we will describe a full deterministic classification of all these events that is expandable to an expert system. We need to specify in detail the different restoration schemes and the manner by which an EMM chooses an appropriate restoration procedure for a classified abnormal event.

14. *New Developments in Neutron Focusing*

H. Chen-Mayer, D.F.R. Mildner, and V. Sharov (X-Ray Optical Systems, Inc.)

Objective: To increase both the elemental sensitivities and the spatial resolution for Prompt Gamma Activation Analysis (PGAA) and Neutron Depth Profiling (NDP) at the NIST Cold Neutron Research Facility.

Problem: In the past both PGAA and NDP have used neutron beams directly from the reactor. The spectrum from the cold source not only has an increased useful flux, but is also shifted to longer wavelengths resulting in higher cross sections for most elements. Nevertheless, small samples have a reduced fluence and therefore reduced signals. However, if the beam current density can be concentrated by focusing, then even higher fluxes are available over a small area.

Approach: All of the useful methods for focusing a white beam of neutrons are based on mirror reflection which is most effective for long wavelength neutrons. Long wavelength neutrons are transported to the instruments by large macroguides. These enter the very narrow cylindrical guides of the polycapillary fibers and are transported by successive grazing angle reflections. Each fiber contains over a thousand 10 μm channels occupying about 10% of the entrance area of the lens. The fibers are curved such that the neutron trajectories paths are bent towards a common focus, where the sample under investigation is placed.

Results and Future Plans: We have developed a focusing lens collaboratively with X-Ray Optical Systems, and placed it at the end of one of the guides at the NIST reactor for PGAA measurements. The lens compresses a neutron beam of cross section 50 x 45 mm^2 and current density of 10^8 cm^{-2} s^{-1} onto a focal spot of diameter 0.53 mm (FWHM) at a distance of 52 mm from the exit of the lens, and with an average gain of 80 in neutron current density. Research and Development Magazine has recognized this lens as one of the 100 most technologically significant new products of 1995.

PGAA measurements demonstrate the enhanced sensitivity and detection limits for various elements and the spatial resolution in one transverse dimension. For two test particles (Gd glass and Cd metal of sizes less than 0.5 mm), the gain in the gamma count rate with the lens is a factor of 60, the gain in signal-to-noise is 6 to 7, and the detection limit is improved by a factor of 20. This improvement is obtained despite the fact that only 3.5% of the neutron beam incident on the lens is delivered to the focus. The spatial resolution at the focus is determined to be better than 0.5 mm by monitoring the boron prompt gamma signal as a row of alternating borosilicate and lead silica glass fibers is scanned across the focal plane. The system can be used for two-dimensional mapping of samples on a submillimeter scale to complement other analytical techniques.

Based on these measurements we have designed a lens which not only focuses but also bends the beam downward out of the direct path of the incident beam. This will result in measurements with further improvements in the signal-to-noise ratio, and therefore the detection limits.

One of our goals is to perform compositional mapping using NDP with a monolithic focusing lens to achieve greater lateral resolution and higher sensitivity. Such a lens will use a greater fraction of the neutron beam incident on the lens and will result in a smaller focal spot. We have performed test measurements to characterize prototype lenses. The best one gives a neutron current density gain of 70 over an area 0.16 mm in diameter (FWHM).

Publications:

Xiao, Q.F., Chen-Mayer, H.H., Sharov, V.A., Mildner, D.F.R., Downing, R.G., Gao, N., and Gibson, D.M., **"Neutron Focusing Optic for Submillimeter Materials Analysis,"** Rev. Sci. Instrum. 65, 3399-3402 (1994).

Chen, H.H., Sharov, V.A., Mildner, D.F.R., Downing, R.G., Paul, R.M., Lindstrom, R.M., Zeissler, C.J., and Xiao, Q.F., **"Prompt Gamma Activation Analysis Enhanced by a Neutron Focusing Capillary Lens,"** Nucl. Instrum. & Meth. B95 , 107-114 (1995).

15. *Neutron Activation Analysis Using Very Short-Lived Isotopes*

***D.A. Becker**, R.M. Lindstrom, J.K. Langland, and R.R. Greenberg*

Objective: To provide a neutron activation analysis (NAA) system which will allow the determination of activation products with half-lives of ≤ 1 second to about 60 seconds with high accuracy.

Problem: There are a number of elements that upon neutron irradiation produce very short-lived activation products which are potentially useful for neutron activation analysis. In some cases these nuclides may be the only available activation product (e.g., for F, O, and Pb); in other cases the nuclides are activation products which provide improved sensitivity, accuracy, or ease of determination (e.g., for Se, Ag, and Rh). Their use would require an irradiation capsule transfer time from the reactor to counting station of 0.5 s or less. Because the existing pneumatic tubes in the NIST nuclear reactor have relatively long transfer times (3 to 15 s) and have no accurate timing capability, these deficiencies make them relatively useless for the measurement of very short half-life activation products.

Approach: The extended shutdown of the NIST reactor for modifications and facilities upgrading provided the opportunity to obtain a new pneumatic tube irradiation facility and insert it into the reactor at an unused irradiation thimble location. This new facility includes a separate control console to provide reproducible and accurately known irradiation times, and with a very short transfer time. Since the NIST shops had already made commitments for construction and modification of other reactor systems during this shutdown, we were required to go outside NIST to obtain this facility.

Results and Future Plans: During FY95 this new rapid pneumatic tube system was designed, constructed, and recently inserted into the NIST 20 MW research reactor in the RT-2 location. This system includes computer controlled irradiation and counting and a 50 sample auto-loader. For design and construction, the system was divided into three portions: (1) the irradiation terminal (the part actually inserted into the reactor), (2) the flight lines and computer controlled irradiation system including the auto loader, and (3) the automated gamma-ray counting and analysis system. This latter portion included a loss-free counting system which allows the reliable determination of short half-life nuclides at very high count rates. All three portions had very stringent design constraints and specifications which required constant interaction and coordination with the contractors.

All three portions of the system have now been received, and portions (1) and (3) have received final acceptance. Portion (1) was inserted into the NIST reactor prior to reactor startup at the end of September, 1995. Final assembly of the three portions and evaluation of the overall system will commence January, 1996, after installation of additional specialized shielding.

Initial evaluation of this new system will include measurement of flight times and repeatability of the entire system, as well as determination of the neutron fluence characteristics and variation in the new RT-2 irradiation terminal. Additional evaluation will include the determination of analytical sensitivities and repeatability for a variety of short half-life nuclides.

Publications:

Becker, D.A., Lindstrom, R.M., Langland, J.K., and Greenberg, R.R., **"The New NIST Rapid Pneumatic Tube System,"** J. of Trace and Microprobe Techniques 14, No. 1 (in press).

Lindstrom, R.M., Ammerlaan, M., and Then, S., **"Loss-Free Counting at IRI and NIST,"** J. of Trace and Microprobe Techniques 14, No. 1 (in press).

Lindstrom, R.M., Becker, D.A., Langland, J.K., and Greenberg, R.R., **"The NIST Rapid Irradiation and Counting System,"** J. Radioanal. Nucl. Chem., Articles (in press).

16. *Improved Measurement Capabilities Afforded by Cold Neutron Beams*

R.M. Lindstrom, R.L. Paul, and G.P. Lamaze

Objective: To upgrade the Prompt Gamma Activation Analysis (PGAA) and Neutron Depth Profiling (NDP) instruments at the NIST Cold Neutron Research Facility.

Problem: PGAA and NDP are techniques for non-destructive chemical analysis of selected elements. The detection limits for different elements depend on the neutron flux and the reaction cross sections. A redesign of the cold neutron source, and reconfiguration of the PGAA and NDP instruments, promise to give nearly an order of magnitude improvement in sensitivity, opening up new application areas.

Approach: During the past year, the NIST reactor has been undergoing major improvements, including the installation of new heat exchangers, a new liquid hydrogen cold source and refrigerator, and additional neutron guides. Both PGAA and NDP are neutron absorption techniques, and absorption cross sections for most elements increase with wavelength. Neutrons from the reactor exhibit a Maxwellian spectrum with a characteristic temperature of ~300 K, or wavelength of ~1.8 Å. The new cold source shifts this spectrum to about 45 K, or wavelength ~4.6 Å. These long wavelength neutrons are taken from the reactor using high-efficiency nickel-coated guides to an area of lower background. Consequently the reaction rate is higher and the background lower than with a conventionally collimated beam of thermal neutrons. This results in greatly improved sensitivities.

A major reconstruction of the PGAA system has been accomplished during the reactor shutdown. A new sample positioning assembly rigidly fixes the sample-detector geometry and will provide better reproducibility. In addition, the sample holder can accommodate a wider variety of sample sizes. Better shielding and collimation will improve the neutron beam shape and more tightly control the field of view of the gamma-ray detector. The interfering radiation from the adjacent neutron guide will also be greatly reduced, and thus the detection limits will improve by more than the increased sensitivities alone. The new variable neutron and gamma-ray collimation greatly increases the dynamic range of measurements of the system. Finally, the spectrometer is completely surrounded by a new shielding enclosure for better personnel radiation protection. Provision has also been made for including a neutron bender-focuser in the analytical system.

The NDP instrument is placed on the NG-0 cold neutron curved guide which has a coating of nickel-titanium supermirror, and gives an increase of about a factor of 3 in neutron current density relative to a ^{58}Ni guide. The chamber has been modified to accept the larger area beam (15 cm^2 vs. 7 cm^2 with the previous beam). This larger area will allow us to take full advantage of a neutron focusing lens planned for this instrument.

Results and Future Plans: For PGAA, the combination of the new cold neutron source and the higher operating power of the reactor (20 MW vs. 15) gives 6 times higher sensitivity for all elements.

At the NDP instrument, the thermal equivalent neutron current density has been measured by a calibrated fission chamber and gold foil activation, and is a factor of 6 greater than the previous level. At the same time the in-beam gamma-ray dose has been reduced by a factor of 2, lowering the overall background, and is especially important for planned measurements of nitrogen-containing thin films.

Publications:

Paul, R.L., Lindstrom, R.M., and Heald, A.E., "**Cold Neutron Prompt Gamma-Ray Activation Analysis at NIST-Recent Developments,**" J. Radioanal. Nucl. Chem. (in press).

17. *Intercomparisons of NIST Definitive Methods and Primary Standards with other National Metrology Laboratories*

R.L. Watters, Jr., *F.R. Guenther, and W.E. May*

Objective: The Analytical Chemistry Division (ACD) is an active participant in key international intercomparisons using definitive methods of chemical analysis. These activities are designed to establish traceability of chemical measurements to the SI unit of the mole through the analysis of primary standards. Such intercomparisons provide a basis for extending the knowledge and experience gained to improve the accuracy and comparability of chemical measurements on more complex materials as well as those using non-definitive methods.

Problem: The need for comparability and traceability of chemical analysis data is becoming recognized worldwide. The identification of global trends in the state of the biosphere and the evaluation of the effects of trace elements in the environment are only possible on the basis of reliable data. A significant proportion of industrial production and international trade is also dependant on analytical chemical measurement. The uncertainty in the validity of many of these measurements means that there is a considerable amount of repeat measurement made, particularly by regulatory agencies on imported products. This is expensive and impedes the free flow of international trade.

Approach: Systems of traceability in the area of chemical measurement are not as well developed and recognized as those in physical measurements, although the two areas are not fundamentally different. The ACD is a key participant in efforts of the International Committee for Weights and Measures (CIPM) and its Consultative Committee on Amount of Substance (CCQM) to address the issue of chemical measurement traceability. The CCQM has begun to examine ways to link chemical measurements to the International System of Units (SI) at the highest levels of national systems of measurement. CCQM member laboratories and other regional chemical metrology alliances such as EURACHEM are responsible for providing the link between chemical measurements in their respective countries and the SI units of the kilogram and the mole. Such traceability can be achieved through a highly leveraged system of key certified reference materials (CRMs), reference methods, secondary reference materials, and strategically selected intercomparisons among national chemical laboratories. ACD both organizes and participates in such intercomparisons to establish comparability of chemical measurements using definitive methods and key primary reference materials.

Results and Future Plans: ACD has organized the CCQM intercomparison of inorganic elements in water using isotope dilution mass spectrometry (IDMS). In the first exercise, only two laboratories (ours and one in China) were able to consistently achieve the target values and uncertainties. ACD is now responsible for writing a protocol with sufficient detail for other participants to use IDMS successfully. The next intercomparison will involve the determination of lead in water.

Another CCQM intercomparison involves the analysis of simple gas mixtures. This exercise is organized by the Netherlands Measurement Institute (NMi). Most of the laboratories engaged in this study are consistently capable of producing data within the target accuracies and precisions. In addition ACD and NMi have an ongoing program for intercomparing primary gas mixtures in order to establish and verify equivalence for designated standards. This arrangement is documented in a formal Memorandum of Understanding between NIST and NMi.

18. *An Expanded NTRM Program Designed to Supplement the Availability of NIST SRMs and Other Primary Gas Mixtures*

W.D. Dorko and F.R. Guenther

Objective: To increase the number and availability of NIST traceable gas standards accessible to end users.

Problem: Traceability in chemical measurements is becoming more important, especially with the increase in foreign trade agreements. Measurements requiring traceability to NIST calibration gas standards have mostly been achieved through the use of gas SRMs. The demand for traceable measurements has increased dramatically, while the ability of NIST to produce gas SRMs has remained constant and insufficient to meet demand.

Approach: To develop a program where the specialty gas industry produces and distributes calibration gas mixtures, while NIST provides sufficient quality assurance to assure traceability to NIST and to meet regulatory and end-user requirements.

In FY95, we devised a plan to improve our gas NIST Traceable Reference Material (NTRM) program, established in FY93 to provide our customers with a more readily available alternative to SRMs. For production of a NTRM, a specialty gas producer manufactures a batch of gas mixtures of specified composition and quality, makes measurements on each mixture and provides all of the data and a selected subset of the batch to NIST for quality assurance measurements, statistical analysis, and value assignment. The producer can then sell them to customers, use the NTRM batch to produce other NIST traceable gases, or produce EPA protocol gas standards.

In the NIST Traceable Reference Material (NTRM) program, the producer determines a need, produces a batch (minimum 10) of identical cylinder mixtures, and analyzes every cylinder. NIST reviews the analytical data and selects cylinders from the batch to be sent to NIST for value assignment. A successful batch is certified by NIST using the producer's analytical data and NIST's value assignment. The producer can use or sell the resultant mixtures as NTRMs. The producer is responsible for monitoring the stability of the NTRM through periodic re-analysis, and submission of the data to NIST. The production and certification process can take as few as four months from perceived need to final product.

Results and Future Plans: Currently, NIST can produce 5 to 6 batches of SRMs per staff-year. This output results in the certification of a maximum of 300 SRM cylinders per year. Under the NTRM program, NIST can produce up to 35 batches of traceable gas mixtures per staff-year. During the past year, six companies produced 59 batches of NTRMs, which represent over 1400 cylinders. These mixtures were primarily used by the specialty gas companies to produce tertiary commercial gas mixtures. Thus, the NTRM program has allowed NIST to leverage available resources into a much larger number of reference materials available to U.S. laboratories.

During FY93-95, all gas NTRMs were directly linked to existing SRMs. However, strong sales of the existing SRMs and popularity of the new NTRMs has limited our capacity to provide the new gas mixture compositions required by industry. Starting in FY96, we will expand the availability of NTRM gas mixtures to include any composition for which we have primary standards. In addition, we will select some SRMs for non-renewal. This strategy will provide the customer with more choices at less cost while maintaining traceablility to NIST primary standards. It will also allow better leverage of NIST resources in providing the traceable standards needed by users and allow redirection of NIST resources into new SRMs. NIST has certified 115 batches of gas mixtures under the NTRM program. These batches represent 2655 NIST traceable gas standards, which industry has leveraged into a minimum of 105,000 EPA protocol gas standards with a value of $38 million. This would not have been possible with the gas SRM program alone due to limitations of production.

Publications:

Guenther, F., Dorko, W., Miller, W., and Rhoderick, G., **"The NIST Traceable Reference Material Program for Gas Standards,"** NIST Special Publication 260-126 (in press).

19. *Health-Related Measurement Quality Assurance Activities*

***J.M. Brown-Thomas**, D.L. Duewer, S.A. Margolis, C.S. Phinney, K.E. Sharpless, L.T. Sniegoski, M.J. Welch; and P.M. Ellerbe, S.E. Long, and S.S. Tai (College of American Pathologists, Guest Researchers)*

Objective: To provide infrastructural support for measurement accuracy and traceability to laboratories performing health-related measurements.

Problem: Inaccuracy in health-related measurements raises overall health care costs, results in misdiagnoses, leads to inaccurate conclusions in clinical studies, and may result in inaccurate nutrition labeling.

Approach: NIST works closely with the College of American Pathologists (CAP), which sponsors three research associates at NIST to work with NIST scientists on development of methods and reference materials to support accuracy in clinical analyses. The CAP operates a large proficiency testing program for clinical laboratories. Analyses performed at NIST using isotope dilution mass spectrometric Definitive Methods are used to evaluate the accuracy of the methods used routinely by clinical laboratories to assess the health status of patients. NIST works closely with the National Cancer Institute to provide measurement Quality Assurance (QA) to over 60 laboratories conducting analyses of serum levels of potential chemopreventive agents in clinical trials. Interlaboratory studies, reference materials, and workshops are used to document and improve the accuracy of the measurements of a number of important micronutrients. In addition, NIST is working with USDA and FDA to provide reference materials to support accuracy and traceability in nutrition labeling on foods.

Results and Future Plans: A new lot of SRM 909, Human Serum, has been certified for twelve important serum constituents. This material is widely used by the clinical laboratory community as a direct traceability link to NIST measurement accuracy. A number of CAP reference and survey materials were also value-assigned using NIST measurement science, thus providing additional vehicles for traceability. NIST efforts coupled with those of industry and other government agencies have resulted in marked improvements in clinical laboratory accuracy and precision for many important health markers. Similar improvements have been observed for the laboratories participating in the QA program for micronutrients. The measurements from selected laboratories are now good enough that their results can be used along with those of NIST for the certification of micronutrients in serum, as was done this past year for SRM 968b, Fat-Soluble Vitamins and Cholesterol in Human Serum.

Future plans include continued cooperation between CAP and NIST for developing new methods and providing NIST traceable materials. Three new frozen serum SRMs will be certified for important serum analytes. Round-robin exercises will continue to be an important part of the QA effort for micronutrients. In an effort to address the suggestion that the program serve as a quality assurance model that addresses a broader range of measurement needs, NIST will hold the next QA workshop in conjunction with the Experimental Biology '96 meeting. Under development are new SRMs for food labeling, including an infant formula material and a composite baby food material certified for vitamins and other important nutrients and a composite food certified for fatty acids and cholesterol.

Publications:

Brown-Thomas, J., Kline, M.C., Schiller, S.B., Ellerbe, P.M., Sniegoski, L.T., Duewer, D.L., and Sharpless, K.E., **"Certification of Fat-Soluble Vitamins, Carotenoids, and Cholesterol in Human Serum: Standard Reference Material 968b,"** Fres. J. Anal. Chem. (in press).

Brown-Thomas, J. and Sharpless, K.S., (Eds) Methods of Analysis of Cancer Chemopreventive Agents in Human Serum. NIST Special Publication 874, Gaithersburg, MD 109pp (1995).

20. *Recertification of SRM 909-Human Serum*

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Objective: To certify a new lot of SRM 909 Human Serum, for 12 clinically important serum analytes.

Problem: Every year, billions of chemical tests are performed on blood and other biological matrices from humans to determine health status. Most of these tests involve quantitative determinations of the concentration of a particular health marker in these matrices. Because of this vast market for tests, many different approaches are in use for the most important analytes, and these approaches often provide different answers. Furthermore, an approach that provides accurate results in one laboratory may be seriously biased in another. These problems may result in inaccurate diagnoses and considerable retesting when changing health care providers. There is a great need for reference materials with known concentrations of important health markers to facilitate the evaluation of the accuracy of the methods being used in the field and to provide accurate controls to laboratories and their suppliers.

Approach: NIST, in cooperation with the College of American Pathologists (CAP), has a long history of providing human serum based SRMs and other reference materials with certified concentrations determined by the most accurate methods known; i.e., Definitive Methods developed at NIST. SRMs for clinical measurements have played an important role in the significant improvement seen in the accuracy of clinical laboratory measurements for such important analytes as cholesterol, glucose, and calcium. This improved accuracy leads to better diagnosis and treatment and to reduced health care costs from reduction in retesting. For all of the organic analytes and most of the inorganic analytes, the definitive methods are based upon isotope dilution mass spectrometry (IDMS). For the organic analytes, the methods involve careful and complex sample preparation followed by analysis by gas chromatography/mass spectrometry (GC/MS). For the inorganic analytes, the sample preparation procedures are very different but equally rigorous. The measurement process for the inorganic analytes involves either thermal ionization mass spectrometry or the much faster inductively coupled plasma (ICP) mass spectrometry. The only exception is sodium, which is determined using a gravimetric procedure. Chloride is the only analyte for which two methods are used for certification; an IDMS method and an equally accurate and precise coulometric method. For this SRM, the certification process involved both NIST Scientists and CAP Research Associates at NIST.

Results and Future Plans: SRM 909b is the third issuance of this freeze-dried human serum material widely used by the clinical laboratory community. This material has two levels, one of which has analyte levels that are generally near the middle of the normal range for human serum while the other has generally elevated levels. Six organic analytes; cholesterol, glucose, uric acid, urea, creatinine, and triglycerides; and six inorganic analytes; calcium, sodium, magnesium, lithium, potassium, and chloride; have been certified in SRM 909b. The expanded uncertainties (95% confidence intervals) for these measurements are very small, less than 1%, for most analytes, demonstrating the precision of the definitive methods as well as the uniformity of the SRM. Information values for other analytes such as bilirubin and creatine kinase were provided by the cooperative efforts of the material manufacturer using standard clinical chemistry autoanalyzer methods. In the near future, NIST will certify additional SRMs for the clinical laboratory community, e.g., frozen serum SRMs for electrolytes, glucose, and cholesterol and triglycerides. Research is continuing on development of new high-accuracy mass spectrometry methods for other important health markers such as enzymes and the iron-containing species in human serum.

21. *Environmental Measurement Quality Assurance Activities*

***R.M. Parris**, M.M. Schantz, T.L. Green, J.R. Moody, J. Smeller, G.C. Turk, T.W. Vetter, L.J. Wood, F.R. Guenther, and S.A. Wise*

Objective: To provide infrastructural support for measurement accuracy and traceability to laboratories performing chemical measurements in environmental monitoring programs.

Problem: Environmental analyses are critical because decision making based on inaccurate measurements or data of unknown quality can have significant economic and health consequences.

Approach: NIST provides quality assurance (QA) activities in support of several environmental monitoring programs. For the past nine years we have worked in cooperation with the National Oceanic and Atmospheric Administration (NOAA) and the Environmental Protection Agency (EPA) to assess the interlaboratory and temporal comparability of data for organic contaminants from laboratories involved in the NOAA National Status and Trends (NS&T) Marine Monitoring Program and the EPA Environmental Monitoring and Assessment Program (EMAP). Since 1991 we have also worked with the National Marine Fisheries Service (NMFS) within NOAA to assess comparability of results for measurements of both organic and inorganic contaminants in marine mammal tissues. In 1993 we initiated a quality assurance activity in support of the EPA National Health Exposure Assessment Survey (NHEXAS), which is intended to provide critical information about the magnitude, extent, and causes of human exposures to environmental contaminants so that informed decisions can be made regarding environmental health risks. In the NHEXAS program three separate field studies are being conducted under cooperative agreements between EPA and three research laboratory consortia to measure various contaminants (trace metals, volatile organics, polycyclic aromatic hydrocarbons (PAHs), and pesticides) in indoor and outdoor air, house dust, and soil. In all three of these programs, NIST provides quality assurance support, including the development of needed Standard Reference Materials (SRMs) and other control materials, coordination of interlaboratory comparison exercises, evaluation of the interlaboratory data, analysis of sample splits with the participating laboratories, and coordination of workshops to discuss the results of these activities. In the interlaboratory exercises the participants use the methods routinely used in their laboratories for the required analyses rather than all laboratories being required to use the same method.

Results and Future Plans: The results from the NOAA NS&T and EPA EMAP QA program are described to illustrate the impact of these activities. For this program, NIST efforts focus on improving the comparability of measurements for over 60 organic contaminants including selected (PAHs), polychlorinated biphenyl congeners (PCBs), and chlorinated pesticides in marine bivalve tissue, sediment, and fish samples. Since 1993, private sector and other laboratories that are not associated with the NOAA/EPA programs have participate in the exercises by subscribing to the "NIST Intercomparison Exercise Program for Organic Contaminants in the Marine Environment." Current participants in these interlaboratory exercises represent a number of multi-laboratory monitoring programs and include over 40 federal, state/municipal, university/college, private sector, and international laboratories. At the beginning of this activity, the NOAA NS&T and EPA EMAP program managers had no tools to assess the comparability and quality of the measurements made by the various laboratories providing data for their monitoring programs, nor could they effectively document changes in the quality of the data produced. With continuous participation in these annual intercomparison exercises, laboratories can now demonstrate the quality and comparability of their results. Two natural matrix SRMs (e.g., sediment and mussel tissue) and six calibration solution SRMs have been developed at NIST in response to the needs of this program. The availability of these SRMs provides the opportunity for laboratories to evaluate their performance on a continuous basis.

22. *Development of Reference Materials to Assess Lead Contamination in Both Indoor and Outdoor Environments*

P.A. Pella, A.F. Marlow, and R.L. Watters, Jr.

Objective: To develop reference materials needed to establish and improve the accuracy of lead measurements in the environment.

Problem: Old paint, soil, and dust can be major sources of lead poisoning in young children. Because of increased demand for accurate analytical methods for measurement of lead in these substances, NIST and other agencies such as the Environmental Protection Agency, the Research Triangle Institute, and the U.S. Geological Survey (USGS) have been working together to provide measurements and standards to meet these needs.

Approach: NIST is developing key Standard Reference Materials (SRMs) with certified values for lead and other important analytes in soil, dust, and paint. Candidate materials are collected by EPA from various abatement projects and sent to NIST for processing. Soils have been collected by EPA, USGS, and NIST. USGS processes candidate soil materials. Target lead levels are specified to cover the range of concentrations impacted by regulations and abatement decision levels. Homogeneity assessments and certification analyses are performed in the Analytical Chemistry Division at NIST with cooperative analyses being provided by USGS in the case of soils. Data from the use of these SRMs with regulatory methods are furnished through the Environmental Lead Performance and Testing (ELPAT) program.

Results and Future Plans: During the past year, substantial progress has been made in the preparation and certification of these SRMs. This year we have finally obtained enough material to process two of the most urgently needed paint SRMs having nominal concentrations of 4% and 0.5%. All of the SRMs that have been planned are in various stages of the certification process with the exception of a high level household dust material containing nominally 1% lead (SRM 2584). This material has been collected, partially processed, and is expected to become available in 1996. A household dust (SRM 2583) contaminated with paint containing lead at a background level of 86 µg/g lead, is nearly ready for distribution.

Other SRMs in the certification analysis stage include the powdered paints: SRM 2589 (nominal 10% lead), SRM 2580 (nominal 4%), and SRM 2581 (nominal 0.5%). SRM 2582 was certified in 1992 and contains the lowest level in this series at about 200 µg/g lead. Two soil SRMs (SRM 2586 and SRM 2587) are contaminated with paint containing lead, at nominal 400 µg/g and 3000 µg/g lead, respectively.

One of two Reference Materials (RMs) scheduled for completion next year is RM 8680, a section of a fiberboard overcoated with a paint layer containing nominally 1-2 mg/cm^2 lead. This RM is intended for testing field methods such as chemical test kits and portable x-ray fluorescence analyzers. Another unique RM consists of a series of simulated human tibia phantoms made from plaster of Paris with lead spiked in at nominal levels of 0, 5, 10, 20, 50, 100, 200, and 300 µg/g lead. This RM is intended to benchmark in-vivo methods for measuring lead in bone.

We also expect to develop a replacement next year for SRM 2579, a series of paint films for calibrating and checking the performance of portable, hand-held, x-ray fluorescence analyzers used in the field. Another soil contaminated with lead from gasoline is also planned.

Publications:

Pella, P.A., DeVoe, J.R., and Marlow, A.F., **"Development of NIST Standard Reference Materials for Lead in Blood, Paint, Household Dust and Simulated Bone,"** in Lead in Paint, Soil and Dust: Health Risks, Exposure Studies, Control Measures, Measurement Methods, and Quality Assurance, ASTM STP 1226, Beard, M.E. and Allen Iske, S.D., (eds), American Society for Testing and Materials, Philadelphia, PA, (1995).

23. *International Collaboration for Value-Assignment of Trace Metals in an Antarctic Sediment*

G.C. Turk and R.L. Watters, Jr.

Objective: To provide an additional tool for assuring the international comparability of key environmental measurements through the certification of a Marine Antarctic Sediment.

Problem: An important element of international comparability for environmental chemical measurements is the use of Certified Reference Materials (CRMs). International cooperation in the development of CRMs facilitates the acceptance and efficacy of such materials.

Approach: International collaboration in the production of new CRMs may be coordinated through international metrological organizations, such as the CIPM or NORAMET. An alternative approach is a selected bilateral agreement between standards laboratories. The latter approach was taken here, through a cooperative agreement between NIST and the Istituto Superiore di Sanitá (ISS) of Italy. Under the framework of the Italian National Program for Research in Antarctica, ISS has worked with NIST, the Institute of Reference Materials and Methods (IRMM), and laboratories in Italy, Hungary, Poland, and Spain to produce a new CRM for Trace Metals in Marine Antarctic Sediment. This is one of a series of planned CRMs which will improve the accuracy of Antarctic environmental monitoring measurements.

Results and Future Plans: Approximately 100 kg of raw material were collected in the Terra Nova Bay during the IX Italian Expedition. This material was pretreated, ground, stabilized and bottled by IRMM at the Geel Establishment of the Joint Research Centre of the European Union. Certification for 13 elements is envisaged. NIST has completed the determination of six of the lower concentration elements by inductively coupled mass spectrometry (ICP-MS). They are As, Cd, Co, Cu, Ni, and Sn.

The experimental plan, followed by all laboratories contributing to the certification, calls for the analysis of five samples of the CRM, with sample dissolution and instrumental analysis of each sample being performed on a separate day. This unique experimental design ensures that all significant sources of variability are replicated sufficiently to allow straightforward statistical data analysis.

A major portion of the ICP-MS analysis involved the study of potential isobaric interferences and the development of appropriate correction procedures. Such interferences arise when the mass-to-charge ratio of other elements or molecules are the same as those of the analyte elements. The complexity of this sample, with measurable signals observed for almost all of the elements, leads to many potential isobaric interferences. The presence or absence of isobaric interferences at the analyte masses was studied using single element solutions of potentially interfering elements at concentrations matching those found in the Antarctic sediment solutions. When an interference was found, a correction procedure was then developed by using the single element interference solution to determine the fractional relationship between the interfering signal at the analyte mass and a parent ion signal of the interfering element. The final results are shown in Table 1.

Table 1. Concentrations and Expanded Uncertainties Determined by ICP-MS in Marine Antarctic Sediment Material

Element	Concentration (μg/g)
As	3.87 ± 0.19
Cd	0.56 ± 0.02
Co	6.99 ± 0.09
Cu	6.13 ± 0.67
Ni	10.83 ± 0.39
Sn	2.43 ± .17

Future plans include our cooperation in the value assignment of other Antarctic matrices, including melted snow, marine waters, and krill.

24. *Certification of Environmental Matrix SRMs for Organic Contaminants*

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Objective: To certify several natural matrix environmental Standard Reference Materials (SRMs) for selected organic contaminants including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl congeners (PCBs), and chlorinated pesticides.

Problem: Natural matrix SRMs that are representative of different environmental samples are needed to assist in the validation of analytical methods for organic contaminants. The supply of SRM 1974, Organics in Mussel Tissue (*Mytilus edulis*), which was first issued in 1990, was recently depleted requiring the reissue of this material as SRM 1974a. SRM 1649, Urban Dust/Organics, which was first issued in 1982 with only a limited number of certified analytes, required recertification to check the stability and to increase the number of certified constituents.

Approach: For both the reissue of SRM 1974a and the recertification of SRM 1649, the goals were to provide certified values for a greater number of analytes and to reduce the uncertainties associated with the certified concentrations compared to the original materials. For the determination of PAHs both materials were analyzed using four different analytical techniques: (1) reversed-phase liquid chromatography with fluorescence detection (LC-FL) of the total PAH fraction; (2) reversed-phase LC-FL of isomeric PAH fractions isolated by normal-phase LC (i.e., multidimensional LC); (3) gas chromatography/ mass spectrometry (GC/MS) of the PAH fraction on a 5% phenyl-substituted methylpolysiloxane stationary phase; and (4) GC/MS of the PAH fraction on a smectic liquid crystalline stationary phase that provides excellent shape selectivity for the separation of PAH isomers. For the determination of PCB congeners and chlorinated pesticides, SRM 1974a was analyzed using gas chromatography with electron capture detection selectivity and using GC/MS.

Results and Future Plans: Using the above approach, certified concentrations were determined in SRM 1974a for 15 PAHs, 20 PCB congeners, and 7 chlorinated pesticides as compared to certified values for only 9 PAHs and no PCBs or pesticides in the previous material. For the PAHs in SRM 1974a the relative uncertainties for the certified values ranged from 4% to 28% with all but two analytes in the 4% to 11% range as compared to 11% to 28 % in the original material. SRM 1974a is the most extensively characterized tissue matrix SRM with 42 certified values and 71 noncertified values (additional PAHs, PCBs, and chlorinated pesticides and aliphatic hydrocarbons, trace elements, and methylmercury). Because SRM 1974a is provided as a frozen tissue homogenate, distribution outside the U.S. is often limited. Therefore, a portion of the frozen tissue homogenate was freeze-dried and will be issued as a second mussel tissue material (SRM 2974).

For SRM 1649 only five PAHs were certified when first issued; however, when reissued this material will have certified values for 22 PAHs with the majority of the values having relative uncertainties in the 3% to 10% range, and noncertified values for 13 additional PAHs. The same analytical approach was used to provide certified concentrations for 10 PAHs in a new material, SRM 1975, Diesel Particulate Extract, which was developed to provide a reference material for both chemical and Ames bioassay activity measurement communities. Information values for the Ames bioassay mutagenic activity of SRM 1975 will be provided based on measurements performed by the Environmental Protection Agency.

Publications:

Wise, S.A., Schantz, M.M., Hays, M.J., Koster, B.J., Sharpless, K.E., Sander, L.C., and Schiller, S.B., ***"Certification of Polycyclic Aromatic Hydrocarbons in Mussel Tissue Standard Reference Materials (SRMs),"*** J. Polycyclic Aromatic Compounds (in press).

25. *Certification of SRMs in Support of Human Nutrition Studies*

***S.A. Wise**, J.M. Brown-Thomas, P.M. Ellerbe, R.R. Greenberg, D.A. Becker, R. Demiralp, K.M. Garrity, E.A. Mackey, K.E. Sharpless, L.T. Sniegoski, M.J. Welch, V.G. Iyengar (Standard Reference Material Program), and S.B. Schiller (CAML)*

Objective: To certify several natural matrix Standard Reference Materials (SRMs) for selected vitamins, carotenoids, fatty acids, cholesterol, trace elements, and other nutrients.

Problem: The importance of nutrition in disease prevention is now widely recognized and many studies are underway to determine which food components have impacts on various disease states. For example, many studies are focusing on the effects of carotenoids, selenium, and fat-soluble vitamins on cancer prevention. The emphasis on nutrition has led to increased requirements for labeling on foods and the food industry is facing increased pressure to document and provide traceability for their nutrition measurements. At present there are only a limited number of NIST SRMs for nutrient measurements and these are primarily for inorganic constituents.

Results and Future Plans: NIST is actively working to provide an increased array of SRMs certified for such important nutrients as vitamins, carotenoids, cholesterol, fatty acids, and minerals as well as for toxic trace elements. We are currently working on five SRMs for selected nutrients: (1) SRM 968b, Fat-Soluble Vitamins and Cholesterol in Human Serum; (2) SRM 1846, Infant Formula; (3) SRM 2383, Carotenoids in Food; (4) SRM 1544, Fatty Acids and Cholesterol in Frozen Food Composite; and (5) SRM 1548a, Typical Diet.

SRM 968b is the third issue of this material that has found widespread use in studies investigating the potential chemopreventive effects of specific vitamins and carotenoids. Certified values are provided for cholesterol, retinol, retinyl palmitate, α-tocopherol, and four carotenoids; information values are provided for an additional 10 vitamins and carotenoids. All of the values for the vitamins and carotenoids were based on NIST measurements using three different liquid chromatographic methods and the combined results from 40 laboratories that participated in an intercomparison exercise. Cholesterol measurements were made using the NIST definitive method.

SRM 1846, Infant Formula, was developed in cooperation with the U.S. Department of Agriculture (USDA), Food and Drug Administration, and the Infant Formula Council in response to the requirements of the Infant Formula Act of 1980, which defines the minimum and maximum levels of nutrients permissible in infant formula. Certification of vitamin, proximate, caloric, and mineral content was based on NIST measurements of selected vitamins and the results from nine outside laboratories.

The three remaining materials are food composite SRMs that were developed for specific nutrient groups. SRM 1548a, Typical Diet, will be a replacement for SRM 1548, Total Diet, and was prepared in conjunction with the USDA. It is a freeze-dried composite of a large variety of different foods representing the total, daily diet consumed by an individual. This SRM will be certified for a number of dietary components such as proximates, major and minor inorganic nutrients, and toxic trace elements. Certification will utilize results from outside laboratories, as well as NIST measurements. SRM 1544, a frozen food composite developed in cooperation with the USDA, is intended for laboratories involved in the analysis of foods for individual fatty acids and cholesterol. Certified values were provided for six fatty acids based on gas chromatography/mass spectrometry (GC/MS) measurements from NIST and GC measurements at three outside laboratories. Cholesterol values were determined using the NIST definitive method, and the proximates were determined based on measurements from three outside laboratories. A third food composite, SRM 2383, is being developed specifically as a material with high levels of selected vitamins and carotenoids. It was prepared and packaged as a typical baby food by Gerber Foods using a NIST-specified mixture of individual food components.