NISTIR 5584

Chemical Science and Technology Laboratory

CSTL Technical Activities 1994

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

March 22 & 23, 1995

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 molecules. 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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Technology Laboratory

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Submitted to the Panel for the
Chemical Science and Technology Laboratory
Board on Assessment of NIST Programs
National Research Council

March 22-23, 1995

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

A. 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.

During the past year, the Chemical Science and Technology Laboratory (CSTL) has continued its strategic planning efforts. This has lead to a revised mission statement and the setting of four organizational goals. As the Nation's Reference Laboratory, the ***mission*** of CSTL 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. This enabling infrastructure is provided to enhance U.S. industry's productivity and competitiveness; assure equity in trade; and improve public health, safety and environmental quality. CSTL provides these infrastructural capabilities 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 development and implementation of advanced process technologies.

Our current activities address important areas within the mission of the CSTL. Some indicators of success in meeting our new mission and goals are Cooperative Research and Development Agreements (CRADAs) and consortia, patents, research publications and talks, and measurement services such as Standard Reference Materials (SRMs), calibrations and Standard Reference Databases (SRDs). Accomplishments in FY94 are summarized in the table below.

NOTE: Certain commercial equipment or materials are identified in this report to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for this purpose.

Div	Pubs.	Talks	Committees[1]	Seminars	Conferences	CRADAs	Patents	SRMs	SRDs	Cals.[2]
830	2	6	23	9	2	0	0	0	0	0
831	81	125	50	35	6	17	4	1	1	0
833	83	82	31	12	2	1	0	3	6	0
834	91	67	95	3	3	8	1	91	0	158
835	39	110	28	19	10	13	1	57	0	79
836	89	131	89	27	10	26	5	1	2	821
837	94	150	66	15	9	6	2	4	3	8
838	108	122	70	16	9	2	4	0	5	99
Totals	587	793	452	136	51	73	17	157	17	1165

[1] Committee totals include 60 editorships

[2] Calibrations were performed for over 400 customers

Division Key:

830	Laboratory Office
831	Biotechnology Division
833	Chemical Kinetics and Thermodynamics Division
834	Inorganic Analytical Research Division
835	Organic Analytical Research Division
836	Process Measurements Division
837	Surface and Microanalysis Science Division
838	Thermophysics Division

There were many noteworthy technical achievements by CSTL scientists and engineers during FY94, examples of which are presented below. More detailed information about these activities can be found in the writeups of the appropriate Divisions (indicated by the numbers in parentheses).

CSTL staff produced a number of outstanding ***research accomplishments*** in diverse areas. Among those were the demonstration of the potential of electrospray ionization mass spectrometry (ESIMS) for quantitative protein measurements, important to diverse areas including biotechnology and health (835); measurements of the density of natural-gas-liquid components and mixtures, resulting in a reduction of a factor of two in their property uncertainties (838); completion of a new degenerate four-wave mixing (DFWM) facility to be used as a remote sensing diagnostic technique to investigate chemical processes occurring in plasmas (833); use of secondary ion mass spectrometry (SIMS) to characterize and pattern self-assembled monolayers on gold and silver thin films (837); development of a mutant subtilisin protein through x-ray crystallography and genetic engineering, in which the calcium binding site and other engineering changes produced a stable protease that will have enhanced activity in detergents (831); accurate determination of the stoichiometry for the calculation of the thermodynamic properties of Mo+Si and W+Si systems, which are used in a number of modern industries (834); and demonstration of temperature programming in micro-sensor array technology for gas sensing applications, allowing for the detection and discrimination among oxygenated species of interest to the automotive industry (836).

CSTL scientists and engineers authored or coauthored nearly 600 ***publications*** and presented nearly 800 ***talks*** at local, national, and international meetings. A commemorative issue in *Analytical Chemistry* on the history of analytical chemistry featured an article on the history of classical analysis from the mid 1600s, asserting that the revival of teaching classical analysis is vital to the interests of U.S. industry. This paper won the prestigious *NIST Condon Award* for the author (834). Chapters on Fluid Dynamics of Agent Discharge, Flame Suppression Effectiveness, and Flame Inhibition Chemistry and the Search for Additional Fire Fighting Chemicals were coauthored in *NIST Special Publication 861* (836, 833 and BFRL). A paper was published in *Environmental Science and Technology* on sources of urban contemporary carbon aerosol, showing that a high fraction of atmospheric carbon-containing aerosols in the Los Angeles basin during summer come from food cooking in restaurants (837). Staff edited the book *Solution Chemistry,* which was part of the International Union of Pure and Applied Chemistry (IUPAC) series on "Experimental Thermodynamics" (833). A paper on fundamental concepts of the critical behavior of fluids and fluid mixtures useful for chemical engineering applications appeared in *Supercritical Fluids: Fundamentals and Applications* (838). This NATO Series book was also edited by CSTL staff (838). The development of a new stationary phase in liquid chromatography which is optimized for the separation of carotenoid isomers was published in *Analytical Chemistry* (835). A paper describing the results of interlaboratory reproducibility studies and statistical analysis of uncertainty of forensic DNA profiling appeared in *Analytical Chemistry* (831, 835, and 837).

Measurement services remain a high priority in CSTL. Nearly 160 ***Standard Reference Materials*** were certified for chemical composition or physical properties. Examples of important work in this are include a polymerase chain reaction (PCR) DNA profiling standard, which will help hasten the transition towards acceptance of PCR-based DNA profiling technology by the criminal justice system (831); certification of uncommon commercial asbestos and quantitative asbestos in building materials, used in the congressionally mandated laboratory accreditation program (837); three SRMs on the heating value of sulfur-containing coals (833); the certification of an aluminum freezing point standard fixed-point cell (836); preparation and certification of eight oxygenates-in-gasoline SRMs to provide quality assurance benchmarks for new reformulated fuels, needed to meet lower automotive exhaust emissions standards (835); and certification of two new SRMs for low electrolytic conductivity, important for the quality of feedwater and boiler water in power plants (834). Among the 17 ***Standard Reference Databases*** released or updated were an upgrade of the NIST/CARB Biomacromolecular Crystallization Database to incorporate the NASA microgravity crystallography data (831); release of the GRI/NIST Orifice Meter Discharge Coefficient Database (836); update of REFPROP, which now calculates equilibrium and transport properties of 38 pure alternative refrigerants and mixtures with as many as 5 components (838); software innovations for the NIST/EPA/NIH Mass Spectral Database (833); and release of version 2.0 of the Desktop Spectrum Analyzer, used extensively in electron probe analysis (837). We continue to provide important ***calibration services*** to ensure measurement traceability for industry and other government laboratories. These services include airspeed, fluid flowrate, humidity, liquid density and volume, and temperature measurements (836); pressure, vacuum, and leak rate measurements (838); value assignment of customer submitted of gas cylinder standards (835); and optical filter transmission for absorption spectrophotometer (834). This year, eight ozone measuring instruments were calibrated for industry and government, and two NIST designed standard reference ozone photometers were built for foreign governments, adding to the existing international network (837); vacuum and leak standards were developed for Sandia National Laboratory and the

Department of the Navy (838); and special liquid and gas flow metering tests were conducted in support of the multiphase ejector expansion refrigeration cycle (836).

CRADAs and ***consortia*** continue to be a significant mechanism for direct interaction with industry. A CRADA was established with Exxon to investigate the properties of worm-like micelles (838). Through a CRADA with the Sadtler Division of BioRad, considerable progress was made on the development of computer software for advanced mass spectrometric search systems (833). In a collaborative effort with Babcock and Wilcox, Inc., we have developed optical measurement technology as a tool for in-situ monitoring of corrosion species and processes in high temperature, high pressure water (836). This year the Consortium on Automated Analytical Laboratory Systems (CAALS) was reorganized and the membership fee reduced to better address the needs of its members and become more accessible to the laboratory automation community (835). A CRADA was established with OPTEX to study optically active films for commercial applications (837). Measurement technology for noble metals in automotive catalytic converters was developed, critically evaluated, and transferred for commercial use through a CRADA with Battelle's Pacific Northwest Laboratories (834). Through a CRADA with SmithKline Beecham, the usefulness of phospholipid/alkanethiol hybrid bilayer membranes as real-time sensors to monitor receptor-ligand interactions directly has been demonstrated (831).

In FY94, CSTL received nine ***patents***, more than in the three previous years combined. Among the patents were corrosion resistant thin-film thermocouples (836); methods for making and using improved microporous hollow fibers, the improved fibers, and the tube bundles constructed of the fibers (838); an x-ray photoelectric emission spectrometry system (837); a sample cell for infrared spectrophotometry (838); a method for correcting spectral data for background noise (834); the desktop spectrum analyzer computer program (837); planar epitaxial films of SnO_2 (836); temperature-controlled, micromachined arrays for chemical sensor fabrication and operation (836); and a liposome immunoanalysis process with high sensitivity and tunable selectivity for measurement of samples of environmental, health, and biotechnology interest (831, 835). Among the more significant ***invention disclosures*** were an optical trap for the detection and quantitation of subzeptomolar quantities of analytes (831); methods and apparatus for drug delivery using supercritical solutions (838); a process for transparent carbon nitride coating (836); and acoustic cavities for measuring thermal diffusivity and viscous diffusivity of gases (838).

Conferences and ***workshops*** were utilized to assess customer needs and determine future program directions. Two related workshops for flowmeter users and flowmeter manufacturers were held to assess flow measurement needs (836). CSTL staff organized a conference to discuss the development of a quality assurance program for marine and atmospheric chemical measurements for the NAFTA countries (834, 835). A workshop was held on "Chromatography, Electrokinetics, and Separations in Porous Media" to define the role of NIST in addressing separations needs of the biotechnology industry (831). Staff were key organizers in the Twelfth Symposium on Thermophysical Properties, and coordinated the workshop on "Water: Its Measurement and Control in Vacuum" (838). The 49th Calorimetry Conference was chaired by CSTL staff (833). Staff co-chaired the Adriatic Research Conference on Lasers in Surface Science (837).

CSTL staff participated in many ***external activities*** to assist industrial, standards, or other government organizations. Staff serve on three key National Science and Technology Council committees: the Committee on Fundamental Science (L. Powell chairs the Biotechnology Research Subcommittee), the Committee on Environment and Natural Resources, and the Committee on Civilian Industrial Technology. These committees have the charge of coordinating research in the Federal Government in their appropriate areas, providing recommendations for commercial implementation of new or existing technologies, and identifying appropriate technology research needs. L. Powell is working with the Biotechnology Industry Organization to develop a technology roadmap for a coordinated, consensus research and technology development plan to accelerate commercialization of biotechnology (831). Through the leadership of W. May, CSTL staff met with representatives of the American Industry/Government Emissions Research (AIGER) organization and agreed to a program of new measurement technology and standards needs associated with the development of next generation "low emission vehicles" (835, 836). C. Powell and other staff are working to develop national (ASTM) and international (ISO, VAMAS) standards and calibration procedures to achieve comparability and traceability in quantitative surface analysis (837). M. McLinden is participating in the third United Nations Environmental Programme technical reassessment associated with the Montreal Protocol on Substances that Deplete the Ozone Layer, the international treaty that regulates the production of CFCs and HCFCs (838). P. Huang is leading a recently constituted international effort under the auspices of the Consultative Committee on Mass of the Bureau International du Poids et Measures (BIPM) to intercompare humidity standards among the national standards laboratories of 12 countries (836). M. Kurylo served as the program manager/program scientist for the 1994 Airborne Southern Hemisphere Ozone Experiment (833). CSTL staff worked with the International Committee of Weights and Measures (CIPM) to propose a cooperative program among leading national metrology laboratories on uniformity and traceability in chemical measurements (834).

Several CSTL scientists received ***awards*** and ***recognition*** for outstanding achievements in FY94. D. Newbury, C. Powell, L. Currie, and M. Moldover were selected to the position of *NIST Fellow.* D. Simons received the Department of Commerce *Silver Medal* for exceptional leadership and innovative accomplishments in quantitative microbeam mass spectrometry; P. Neta received the DoC *Silver Medal* for exceptional scientific leadership and internationally-acclaimed research on the mechanisms of solar energy storage; and W. Haynes received the DoC *Silver Medal* for exceptional leadership and technical contributions to the world's preeminent research program on the properties of industrially important fluids. R. Perkins received the Department of Commerce *Bronze Medal* for developing state-of-the-art techniques for measuring thermal conductivity of highly polar and electrically conducting fluids; E. Beary and P. Paulsen received the DoC *Bronze Medal* for the advancement of isotope dilution inductively coupled plasma mass spectrometry in the areas of advanced materials and the environment; and D. Mildner, G. Downing, and H.Chen-Mayer received the DoC *Bronze Medal* for the advancement of the theory and the development and realization of neutron focusing lenses with applications in semiconductor characterization. D. Newbury and R. Leapman (NIH) received the NIST *Samuel W. Stratton Award* for developing the unprecedented capability to measure 2-5 atoms at nanometer spatial scales. C. Beck received the NIST *Edward U. Condon Award* for distinguished authorship of "Classical Analysis, A Look at the Past, Present, and Future". G. Burns, M. Kaeser, G. Strouse, C. Croarkin (CAML) and W. Guthrie (CAML) received the NIST *Allen V.*

Astin Measurement Science Award for producing the internationally recognized reference functions for all standard thermocouples. B. Diamondstone (Quality Office, formerly with CSTL), S. Dittmann (Calibration Services, formerly with CSTL) and D. Olson received the NIST *Safety Award for Superior Accomplishment* for the development of a computerized chemical inventory and labeling system. NIST *SRM Measurement Service Awards* went to G. Strouse, C. Beck, K. Pratt, D. Becker, E. Steel, D. Hues, S. Turner, J. Verkouteren, E. Windsor, and J. Phelps (MSEL, formerly CSTL). J. Ladner, S. Outcalt, and M. McLinden received NIST *SRD Measurement Service Awards.* A. Miiller received the NIST *Calibration Measurement Service Award.* T. Gallagher and G. Gilliland received the CSTL *Technical Achievement Award* for their paper "Calcium-Independent Subtilisin by Design". ASTM Committee E-42 has announced a new Award, named the *Cedric Powell Award* "....to be given to a member or participant in ASTM E-42 for contributions to the national or international establishment of standards for surface analysis...". This award was established to recognize Cedric for "..a lifetime of scientific and technical excellence in pursuit of national and international standards for surface analysis." A. Gupta, C. Presser, J. Hodges, and T. Avedisian (Guest Researcher) received a best paper award from the *American Institute of Aeronautics and Astronautics* (AIAA) for their paper "The Role of Combustion on the Transport of Droplets in Pressure-Atomized Spray Flames". M. Moldover was elected a *Fellow of the American Physical Society* for his pioneering research in low temperature physics, critical phenomena, interfacial phenomena, and acoustic metrology. J.M.H. Levelt Sengers was named an *Honorary Fellow* of the International Association for the Properties of Water and Steam. J.M.H. Levelt Sengers, W. Haynes, L. Phillips, B. Stevenson, and C. Thomas were commended by the American Society of Mechanical Engineers for their outstanding contributions to the *12th Symposium on Thermophysical Properties.* R. MacDonald was honored for her outstanding service to the *NIST Chapter of Sigma Xi.*

As this overview indicates, we strive to achieve a balance between providing essential measurements and technology, and carrying out basic research to ensure a healthy science and technology base for the future. Each Division in CSTL is responsible for basic and applied research, and for maintaining close contacts with appropriate industrial and scientific communities.

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

B. Outputs and Interactions (Chemical Science and Technology Laboratory)

1. Publications

Presser, C., Gupta, A.K., Avedisian, C.T., and Semerjian, H.G., "Effect of Dodecanol Content on the Combustion of Methanol Spray Flames," Atomization and Sprays 4, 207-222 (1994).

Presser, C., Gupta, A.K., Semerjian, H.G., and Avedisian, C.T., "Droplet Transport in a Swirl-Stabilized Spray Flame," J. of Propulsion and Power 10, 631-638 (1994).

2. Talks

Semerjian, H.G., "The 'New' NIST," Federal Interagency Chemistry Representatives Annual Meeting, Arlington, VA, February 9, 1994.

Semerjian, H.G., "The Government's New S&T Power Structure...How Can CCR Make an Impact," Council on Chemical Research Special Planning Meeting, Washington, DC, February 10, 1994.

Semerjian, H.G., "Chemical Science and Technology at NIST," 1994 Symposium on MASINT Research & Development for Proliferation Management, Patrick Air Force Base, FL, February 22, 1994.

Semerjian, H.G., "Environmental Technologies and related Standard Reference Data and Standard Reference Materials," U.S.-China S&T Joint Commission Meeting, NIST, Gaithersburg, MD, April 11, 1994.

Semerjian, H.G., "Chemical Science and Technology Programs at NIST", Meeting of the Board on Chemical Science and Technology, National Research Council, Washington, DC, April 24, 1994.

Semerjian, H.G., "Environmental Technologies in CSTL," NIST/NOAA Meeting on Environmental Technologies, NIST, Gaithersburg, MD, August 29, 1994.

3. Committee Assignments

B.I. Diamondstone

American Chemical Society Committee on Chemical and Public Affairs Subcommittee on Research and Science Policy
ASTM Committee D34, Hazardous Wastes
ASTM Committee E-01, Hazardous Wastes

ASTM Committee E-01.01, Ferrous Metals
ASTM Committee E01.20, Fundamental Practices (Secretary)
Analytical Laboratory Managers Association
Council of Chemical Research
Directors of Industrial Research - Analytical Group

H.G. Semerjian

AIChE Engineering Sciences and Fundamental Group, Area 1b. - Kinetics, Catalysis and Reaction Engineering
AIChE Food, Pharmaceutical and Bioengineering Division, Area 15C - Biotechnology
ASME K-11 Committee on Heat Transfer on Fires and Combustion Systems
Combustion Institute - 24th Symposium (International) on Combustion, Program Subcommittee
Council for Chemical Research
    Governing Board
    1994 Program Committee
    University/Industry/Government Interaction Committee
Directors of Industrial Research - Analytical Group
Environmental Technologies Working Group, Dept. of Commerce
Environmental Technology Initiative, Environmental Protection Agency (EPA)
    Pollution Prevention Committee
    Environmental Technologies Committee
International Conference on Liquid Atomization and Spray Systems
    ICLASS-94 - Organizing Committee
    National Science and Technology Council
    Committee on Environmental and Natural Resources, Joint Subcommittee on Environmental Technologies
    Committee on Civilian Industrial Technology

4. Editorship

B.I. Diamondstone

Managing the Modern Laboratory, Editorial Advisory Board

5. Laboratory Colloquium Series

October 13, 1993

Dr. H.F. Dylla, CEBAF/SURF, College of William and Mary, Williamsburg, VA, President, American Vacuum Society, "Surface Processing with Light: Can UV Photons be Made Cheap Enough?"

November 10, 1993

Professor M. Robbins, Department of Physics, Johns Hopkins University, Baltimore, MD, "Simulations of Friction at the Molecular Level."

December 15, 1993

Dr. J.E. Bjorkholm, AT&T Bell Labs, Murray Hill, NJ, "Overview of EUV Projection Lithography: A Quest for 0.1 micron Lithography."

January 19, 1994

Dr. H.F. Winters, CARB/NIST Biotechnology Division, Gaithersburg, MD, "The Spectroscopy of Uracil Radicals."

March 9, 1994

Professor K.R. Wilson, Chemistry Department, University of California, San Diego, CA, "Observing and Controlling Molecular Dynamics in Chemical Systems: A Multimedia Demonstration."

April 22, 1994

Professor A. Zewail, Arthur Ames Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA, "Atoms and Molecules in the Femtosecond Age." Special Joint NIST Staff/CSTL Colloquium.

May 10, 1994

Professor J.T. Yates, Surface Science Center, University of Pittsburgh, Pittsburgh, PA, "Chemistry on Semiconductor Surfaces."

June 8, 1994

H. J. M. Hanley, Thermophysics Division, NIST, Boulder, CO, "Liquid Research in the '90's."

September 7, 1994

D. Denman, Computer Science Center, University of Maryland, College Park, MD, "Illusion, Delusion, and Data: Visualizing Information without Getting Fooled."

6. Conferences/Workshops Sponsored/Co-Sponsored

January 12, 1994

Workshop on Frontiers in Chemistry and Technology for Prince George's County High School Chemistry Teachers, NIST, Gaithersburg, MD (D.A. Olson)

July 12, 1994

Maryland State Governor's Academy for Mathematics, Science, and Technology, NIST, Gaithersburg, MD (D.A. Olson)

I. Biotechnology Division (831)

Lura J. Powell, Chief

A. Division Overview

The Biotechnology Division provides NIST with a cohesive biotechnology effort focussed on the most critical measurement needs of the biotechnology industry, fosters collaboration among NIST scientists conducting biotechnology research, and raises the visibility of NIST contributions to biotechnology research, standards, and data leading to collaborations with industry, universities, and other government agencies. The mission of the NIST Biotechnology program is to advance the commercialization of biotechnology by developing the scientific/engineering technical base, reliable measurement techniques, and data to enable U.S. industry to quickly and economically produce biochemical products with appropriate quality control. During FY94, in addition to research, the Division has been involved in a number of external activities which will assist the private sector in commercializing biotechnology research. The Division has continued interactions with the Biotechnology Industry Organization (BIO). We are currently working with BIO to develop a technology roadmap, a process to develop a coordinated, consensus research and technology development plan to accelerate commercialization of biotechnology. The Division actively participates with the ASTM Committee E-48 on Biotechnology. Division members serve as 1st Vice Chair of E-48, as Chair of the Subcommittee on Terminology and participate as members on other subcommittees. Division staff are working with ASTM to implement recommendations from the 1993 workshop on standardization needs held at NIST. In August, 1994, the Division sponsored a workshop on separations to assess industry needs and help us refocus our separations effort. The Division also cosponsored, with NSF, a workshop on enzymes that operate in extreme environments, an area which could lead to novel biocatalysts. In addition, the "Workshop on Tissue Engineering: From Basic Science to Products", cosponsored with NIH, NSF and FDA, was planned and will be held at NIST on November 22, 1994. The Biotechnology Division continued to play a major role in the planning and coordination of Federal biotechnology research through leadership in the Biotechnology Research Subcommittee (BRS) of the Federal Coordinating Committee on Science, Engineering, and Technology (FCCSET).

In FY94 the Division received major new funds to continue those projects that had been initiated several years ago with competence-building funds provided by the Director of NIST. In addition, funds were received associated with the multi-laboratory National Information Infrastructure initiative, and a new competence-building project in advanced computational biotechnology was started within the Division using funds allocated by the Director's office.

In April 1993, the Consortium on Advanced Biosensors (CAB) was created to address the needs of the biosensor industry and the first research project of the Consortium was initiated in July, 1993. CAB currently has seven industrial members and one Federal agency member. The Consortium has received broad coverage in the scientific press and discussions are underway with other companies interested in joining CAB. Two meetings of the CAB have been held over the past year to share research results with the membership. Some important NIST research results pertaining to non-specific binding of proteins have been achieved which the companies will be able to incorporate into their products.

During FY94, the Division executed eight new Cooperative Research and Development Agreements (CRADAs). Several other CRADAs are under negotiation. The Division also filed one patent disclosure during the year and is working closely with the NIST Office of Technology Commercialization to license existing patents.

During FY94, the Division was reorganized to create a DNA Technologies Group to address this burgeoning area of biotechnology. In addition, a new group leader, Dr. Vincent Vilker was recruited to lead the bioprocess engineering effort in the Biophysical Measurements Group. A reorganization package was submitted to reflect these changes and to rename the groups to describe more accurately their functions. The Biotechnology Division is organized into four Groups: (1) DNA Technologies (formerly Biochemical Measurements) (2) Bioprocess Engineering (formerly Biophysical Measurements) (3) Structural Biology (formerly Advanced Research in Biotechnology) and (4) Biosensor Technology (no change). The Structural Biology Group is located off-site at the Center for Advanced Research in Biotechnology (CARB) on the University of Maryland Shady Grove campus. CARB is a joint venture between NIST, the University of Maryland and Montgomery County, Maryland.

The primary research efforts of the Biotechnology Division and some highlights for FY94 are outlined below:

DNA Technologies

DNA Profiling: Methods and standards are being developed to accurately characterize DNA profiles for forensic and other human identification uses. In FY94 the final validation of materials was completed for a new standard reference material, SRM 2391, which is a PCR-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 now widely used in standardization and quality assurance of forensic testing using methods based on restriction fragment length polymorphisms (RFLP).

DNA Sequencing: Specific reference materials and development of technical expertise are required in the areas of DNA related technologies that are essential for DNA genomic research in the public and private sector. Given that sequences submitted to the genome database have potential errors, and that these errors are significant (one publication suggests that about 4% of the database may have errors), there is a clear need for quality assurance. This year, an automated sequencing laboratory was initiated with the installation of state-of-the-art fluorescence-based sequencing equipment that will be used for many research projects. A program to develop a quality assurance standard for DNA sequencing is underway. NIST is also providing quality assurance expertise to the developers of technology that proposes to use DNA recognition sites on silicon chips for the diagnosis of human genetic diseases.

DNA Damage and Repair: Methods have been developed to characterize DNA damage on a molecular scale using GC/MS techniques. Studies of both *in-vivo* and *in-vitro* systems are underway to understand both damage (as low as one base per million) and repair mechanisms. During the past year, the measurement methods developed in this laboratory have been used to examine the role of antioxidant enzymes that reduce the level of oxidative DNA damage in tissues due to free radicals, and thus provide protection against cancer-causing agents.

Bioprocess Engineering

Biophysical Property Evaluation: Thermophysical and thermochemical properties are being obtained, evaluated, codified and modelled for biochemicals, proteins and biosolutions of interest to biotechnology. These data will be used by the bioengineer to both optimize existing processes and to evaluate proposed processes. In FY94 detailed reviews on two major classes of enzymes, the transferases and hydrolases, have been completed.

Biocatalysis: In September 1994, Dr. Vince Vilker joined the Division as leader of the Bioprocess Engineering group. He has initiated a research program aimed at solving technical roadblocks in the commercial use of P450 enzymes in chemical manufacturing. Investigations are currently focused on 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.

Separation and Purification: Research is underway on new chromatographic processes for separating biomolecules from production broths. Chromatography model development (and validation) is underway in order to help industry meet new process specifications brought on by the increasingly demanding regulatory environment. In August 1994, a Division-sponsored workshop on separations was held at NIST to help us assess industry needs in order to refocus our separations effort.

Biosensor Technologies

Sensor Technologies: NIST develops generic sensor technologies utilizing both optical and electrochemical approaches for applications in clinical laboratories, bioprocessing and environmental monitoring. In FY94, Dr. John Kasianowicz completed his NRC postdoctoral appointment and accepted a position at NIST to pursue research on a novel biosensor technology based on self-assembling proteins for pore formation.

Biomolecular Electronics: The light-sensitive protein, bacteriorhodopsin, is being studied as a potential source for the storage and retrieval of information. This protein, when exposed to light, changes color, representing a change in transition state and storage or release of a byte of information. Studies are underway to understand the mechanism of this change in transition state and to develop methods of immobilizing this protein to increase its stability.

Consortium for Advanced Biosensors (CAB): The studies of the Consortium are of an interdisciplinary nature and ones which most industrial companies do not have the instrumentation and expertise to carry out. The research programs are chosen by the Consortium members and supported through yearly membership fees. In FY94, significant progress was made towards understanding non-specific binding of proteins to surfaces by examining the binding of prototypical proteins to derivatized self-assembling monolayers (SAMS). Dr. David Vanderah joined the Biosensor Technologies group in early FY94 to develop synthetic organic chemistry capabilities which are currently being applied to SAM technology.

Structural Biology

Protein Crystallography: Active programs are underway to obtain the protein structure, using X-ray and NMR techniques, of prototypical proteins, enzymes, enzyme-substrate complexes and model DNA systems. Other efforts include the development of a machine readable database for protein crystallization that aids researchers in the development of new crystallization strategies. Version 3.0 of the NIST/NASA/CARB Biological Macromolecule Crystallization Database (BMCD) was released in FY94 and now contains data from the NASA Protein Crystal Growth Archive.

Protein Folding: Computational and experimental methods have been developed to determine the thermodynamics, cooperactivity, and other parameters describing the energetics of protein folding. In December 1993, Dr. Kevin Ridge joined the Structural Biology group to initiate a program using physical and biochemical methods to understand the structure, folding, and signal transduction of membrane-embedded proteins such as rhodopsins.

Computational Chemistry and Modelling: Quantum mechanical formalisms involving reaction fields are being developed to model the energetics and dynamics of interactions between substrates and active sites of enzymes. Modelling techniques to understand the relationship between protein sequence and structure are being developed. In August 1994, Dr. Michael Gilson joined the Structural Biology group where he will study molecular recognition processes as part of a new competence-building program in advanced computational biotechnology.

Several Division staff members received awards over the past year. Dr. Travis Gallagher and Dr. Gary Gilliland, along with Dr. Philip Bryan of UMD/CARB, received the CSTL Technical Achievement Award for their protein engineering work that lead to enhanced stability and removal of the calcium dependence of the widely-used detergent enzyme, subtilisin. Dr. Jane Ladner received a NIST Measurement Services Award for the incorporation of NASA microgravity crystallization data into a major upgrade of the NIST/NASA/CARB Macromolecular Crystallization Database.

Future Directions

The future needs of the biotechnology industry go beyond the scope of current Division programs. Included in Division plans are the development of programs in biomolecular materials, including biomimetic materials, which will provide novel new products with performance characteristics superior to materials that exist today, and molecular electronics, which will find applications in molecular computing and high density data storage as well as switching, gating and holography. In addition, the Division is planning program expansions to meet industry needs in DNA technologies and biocatalysis.

The current CARB facility is filled to capacity and plans are underway for expansion in cooperation with the University of Maryland. The present CARB facility is 38,000 square feet, which includes 18,000 square feet of research space and 20,000 square feet of conference facility and office/administrative space. A major expansion, CARB-II (80,000 square feet), will be initiated in 1998. An interim expansion, CARB-IB (30,000 square feet), is in the FY96 University of Maryland capital budget and will provide laboratory and office space for 11 additional tenure-track faculty as well as a high field NMR facility. The design phase of this expansion is underway and occupancy is expected in mid-1996. Proposed areas of research for CARB-IB include expanded high-field NMR studies of biomolecular structure, neutron scattering studies of biomolecular structure and dynamics, peptide and biomimetic chemistry, and mechanistic enzymology.

B. Selected Technical Reports (Biotechnology Division)

1. Initiation of an Automated DNA Sequencing Program at NIST

B.C. Levin, K. McKenney, C. O'Connell, P. Reddy, and D. Reeder

To advance the development of standard reference materials and quality assurance guidelines for DNA sequencing, a state-of-the-art automated DNA sequencer has been installed for use in several key projects. The characteristics of this system are (1) fluorescent compounds are used instead of radioactive-labeled compounds, (2) sequencing products are run in one lane, and (3) the software automatically analyzes and prints the data as four color plots with correlated base calls. The system is currently being used in the following projects: (1) Evaluation of Alternate Enzymes and Additives to Improve Sequencing of Mitochondrial DNA by B.C. Levin, H. Cheng, C. O'Connell, D.J. Reeder, and M. Holland. The results from this collaborative effort of the Biotechnology Division, Geocenters, Inc., and Armed Forces DNA Identification Laboratory (AFDIL) were presented at the Fifth International Symposium on Human Identification, Scottsdale, AZ, Oct. 8-12, 1994. One impact of this study has been a change in the standard operating procedures used by AFDIL to sequence mitochondrial DNA. The sequencing of mitochondrial DNA is especially important for human identification in cases where the genomic DNA is not available or has been degraded, e.g., in the identification of the MIAs from Vietnam. (2) The gene for adenylyl cyclase (cya) from Mycobacterium *smegmatis* has been sequenced by P. Reddy and sequencing of the cya gene from Mycobacterium *tuberculosis* shall follow soon. In addition, many site-directed mutants of the regulatory protein IIA of adenylyl cyclase have been created to understand the protein's structure-function relationship. The mutations were confirmed by the automated sequence analysis. (3) Development of DNA Sequencing Standard Reference Materials (SRMs) by K. McKenney, J. Tian and P. Reddy. The automated DNA sequencer is being used for the development of SRMs for DNA sequence determination. Two different classes of DNA SRMs have been designed, constructed and characterized. The first class, called "challenge sequence", has sequences of defined complexity to test and measure the different parameters (hardware, software and wetware) that contribute to the accurate determination of a DNA sequence. The second class consists of true "reference sequences" that function as internal controls for automated DNA sequence determination. Molecular tags that uniquely identify each NIST DNA SRM molecule have been designed, constructed and demonstrated as well. The sequencer has been used for these first generation SRMs to demonstrate their utility and provide the scientific and technical foundation for development of second and third generation DNA sequencing SRMs. These SRMs will prove useful to the large number of laboratories involved in DNA sequence determination including pharmaceutical and biotechnology companies, government labs (HHS, FDA, DOD, DOE, AG, DOJ), university labs, and instrument manufacturers.

2. Quality Assurance of PCR-based DNA Profiling Analysis

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

Polymerase Chain Reaction (PCR) technology enables the rapid and efficient amplification of minute quantities of DNA. Depending on whether a DNA profiling technique is used in a forensic, paternity or research setting, the tissue source of DNA can vary. As with all profiling methods, assuring the quality of the analysis is critical for establishing confidence and ensuring interlaboratory comparability. Two major quality assurance related efforts were pursued during FY94: 1) Validation of SRM 2391 materials and 2) Collaboration with the Armed Forces DNA Identification Laboratory (AFDIL).

SRM 2391 is a PCR-based DNA profiling standard developed for the forensic and paternity testing communities. The SRM set includes 1) a standardized allelic ladder for the genetic locus D1S80; 2) a DNA-based molecular size ladder; 3) PCR-amplified products for the D1S80 locus; 4) Ten genomic DNA samples; and 5) Two cell lines included as intact cells spotted on Schleicher & Schull type 903 paper, to be used as an extraction standard.

Development of SRM 2391 was initiated in FY93. Our FY94 efforts focused on validating the proposed components through two extensive interlaboratory studies. Twenty-three private, state and federal labs in the United States and Canada participated in at least one or more of the interlaboratory studies. All proposed components of SRM 2391 were validated in these studies. As a result of these studies, we found that some commonly used methods often gave miscalls in typing. Changes in operations by some of the laboratories to a common format resulted in consensus. Information on the following genetic systems will be included in the certificate for SRM 2391: D1S80, HLA-DQα, Amplitype PM, HUMTH01, HUMCSF1PO, HUMF13A01, HUMBFXIII, HUMFESFPS, and HUMVWFA31. We expect SRM 2391 to be available from NIST by January 1, 1995.

Our second QA effort was the ongoing collaboration with AFDIL. AFDIL has the responsibility of establishing and maintaining a DNA repository of reference DNA samples for military personnel. To assure the blood stains collected are valid, NIST and AFDIL monitor 100 subsamples from collected bloodstain cards on a monthly basis. 3.18 mm (1/8 inch) diameter, round punched samples are tested for DNA extractability from the bloodstain card. Additionally, we test the extracted DNA for its ability to be amplified by the PCR method. Such procedures test the quality of the extracted DNA for acceptable DNA typing. In FY94, NIST tested 1328 samples by methods that included the following genetic loci: AmpliType PM (284 tests), HLA-DQα (104), D1S80 (836), and HUMTH01 (104). When NIST and AFDIL compared 400 of the typing results, there was 100% agreement for all typing results between the two laboratories. Except for AmpliType PM and HLA-DQα, NIST and AFDIL use different technologies for the DNA typing, thus demonstrating the robust nature of the identification methods and loci used.

3. DNA Base Damage and Antioxidant Enzyme Activities in Human Benign Prostatic Hyperplasia

M. Dizdaroglu, T. Zastawny (University Medical Sciences, Bydgoszcz, Poland) and R. Olinski (University Medical Sciences, Bydgoszcz, Poland)

Oxidative DNA damage induced by free radicals is thought to play a causative role in carcinogenesis. Antioxidant enzymes protect cells against toxic effects of free radicals. There may be a link between activity levels of these enzymes and the level of oxidative DNA damage in carcinogenesis.

The benign prostatic hyperplasia (BPH) is a disease of the prostate gland. Clinically, there is no causal relationship between prostate cancer and BPH. Thus, BPH is not considered to be a premalignant condition. However, most patients with prostate cancer also have BPH. Furthermore, similar phenotypic events occur in progression of normal cells to BPH and cancerous cells. Since BPH may be predisposed to become malignant, it is of great interest to study typical hydroxyl radical-induced DNA lesions in BPH because of the possible role of such DNA lesions in carcinogenesis.

During FY94, we studied DNA base damage and activities of antioxidant enzymes in human BPH tissues and surrounding disease-free tissues removed from prostate glands of 15 patients. In these tissues, endogenous levels of various typical hydroxyl radical-induced products of DNA bases and activities of catalase and superoxide dismutase were measured. The majority of patients had higher levels of DNA base lesions and lower activities of enzymes in BPH tissues than in normal prostate tissues. When activities of both enzymes were lower in BPH tissues than in normal tissues, the increases in the amounts of DNA base lesions over control levels were most prominent. In the case of similar enzyme activities in both BPH and normal tissues, no changes in levels of DNA base lesions were observed.

The results suggest a possible association between antioxidant enzyme activities and levels of DNA base lesions in BPH tissues. Some of the identified DNA lesions are known to be premutagenic and may play a role in carcinogenesis. BPH patients with both decreased antioxidant enzyme activities and increased levels of DNA lesions may be at risk of developing prostate cancer.

In FY95, DNA damage in blood cells of radiation therapy patients will be studied. This is relevant to high incidence of secondary malignancies, most notably leukemia, in cancer patients undergoing radiation therapy. Enzymatic repair of DNA damage by a variety of DNA repair enzymes will be studied. This may help understand DNA repair mechanisms and discover novel activities of repair enzymes.

4. DNA Standards for Capillary Electrophoresis

D.H. Atha and H. Namkung (Project Seed Student)

Capillary electrophoresis (CE) is a relatively new technique which is becoming recognized as a powerful tool for the characterization of DNA. It has numerous advantages over conventional methods such as slab gel electrophoresis in that it is fast, highly reproducible, and easy to automate. CE, like slab gel electrophoresis, requires standards to maintain quality assurance. However, the higher accuracy and precision of CE requires the development of DNA standards specific to CE.

We have used CE to evaluate commercial DNA size standards and have found that it can provide an efficient assessment of size. However, the accuracy of the determination is adversely affected by anomalous retention times due to specific interactions with the gel matrix as well as heterogeneity and conformational effects of the DNA. These anomalous retention times have been shown to be highly dependent on separation conditions, including the choice of gel matrix. For example, we have found that we can minimize the anomalous retention times observed in a one kilobase standard DNA ladder using a preparation of non-gel hydroxyethyl cellulose as the sieving matrix in the capillary. In addition, the DNA sequence heterogeneity that is observed as peak splitting is totally eliminated by this choice of sieving system.

In FY95, we plan to use information obtained on the effects of DNA conformation and separation conditions to design standards required for detection of DNA point mutations. These point mutations produce conformational changes in single stranded DNA and cause a mobility shift that can be resolved by CE. We will examine DNA point mutations using capillary electrophoresis to determine separation conditions which produce the highest resolution and reproducibility. These conditions will then be used in the evaluation of standards for specific diagnostic uses.

5. Evaluation of Q-PCR in Detection of Melanoma Gene Expression

C.D. O'Connell, A. Juhasz (Semmelweis Medical University of Budapest, Budapest, Hungary), and R. Hoch

Increased sensitivity and quantitation of analytical tests used in biotechnology are goals of many laboratories. In response to requests by the John Wayne Cancer Center, we sought to solve these fundamental assay problems as they pertained to RNA and DNA diagnostics. The diagnostic assay that we used for this study was reverse transcription polymerase chain reaction (RT-PCR). This assay can be used to detect small numbers of cells of any lineage by amplifying tissue-specific mRNAs expressed by that lineage. The technique has therefore proven useful in the detection of primary or metastatic cancers. We have used tyrosinase primers to specifically amplify tyrosinase mRNA expressed by the M12 melanoma cell line in a background of mRNA from a breast cancer cell line. A newly developed system, Q-PCR, was used for this investigation. This system can specifically detect and quantitate PCR products through electrochemiluminescence. In the protocol, a biotinylated PCR product is hybridized to a tris

(2,2'-bipyridine) ruthenium (II) chelate- (or TBR-) labeled oligonucleotide probe and the resulting hybrid is captured on magnetic beads for activation of the TBR and quantitation. The hybridization of the tyrosinase DNA probe to the PCR product confers specificity to the reaction, and quantitation is achieved when the TBR-labeled probe emits light after oxidation occurs following a voltage ramp. The protocol is significantly quicker and less labor-intensive than gel electrophoresis followed by Southern transfer, hybridization and autoradiographic detection commonly used to detect specific PCR products. It has the additional advantage of quantitating the PCR samples simultaneously.

We have used Q-PCR to reliably detect the expression of the melanoma-specific gene tyrosinase in the M12 cell line within a background population of cells. In all experiments, tyrosinase-specific RNA isolated from one melanoma cell in a background of 10^5 cells was detected. Using a nested PCR reaction with 1 ug RNA and Moloney Reverse Transcriptase, we were unable to detect a luminescence signal on further dilution of the melanoma line. We improved sensitivity significantly through the use of rTth for reverse transcription. In three experiments, one melanoma cell in 10^6 was detected from a single 35 cycle PCR reaction, and one in 10^7 cells was detected in one of the three experiments. During FY95 we will seek to achieve increased sensitivity and quantitation through the use of alternative instrumentation and assay systems. Experiments utilizing the 373 Automated Sequencer with accompanying Genescan PCR analysis software are in progress.

6. Gene Hunt for the Calmodulin-Like Protein in Mycobacteria

P. Reddy, K. McKenney, P.U. Sarma (Centre for Biochemical Technology, Delhi, India), and P.S. Murthy (University College of Medical Science, Delhi University, Delhi, India)

Correlation exists between the abundance of calmodulin like protein (CAMLP), glucose effect, lipid metabolism, growth of mycobacteria and antitubercular activity of trifluoperazine, a calmodulin antagonist. The antitubercular activity of trifluoperazine prompted an investigation on the characterization of the potential interaction between trifluoperazine and CAMLP. We have begun the cloning of the structural gene for CAMLP from *Mycobacterium smegmatis* to understand its role as a growth regulator in mycobacteria, and to overproduce the protein for studies on biochemical characterization of the interaction between CAMLP and trifluoperazine. The strategy for cloning the structural gene for CAMLP was to purify the protein to homogeneity, determine the amino terminal and internal peptide sequence, design and synthesize degenerate oligonucleotides, and carry out polymerase chain reaction (PCR) on the chromosomal DNA to obtain a DNA probe for cloning full length gene.

CAMLP was purified to homogeneity from *Mycabacterium smegmatis*. One μg of pure CAMLP was obtained from 70 g of cells. The purification involved ammonium sulfate fractionation, chromatography on Sephadex G-75 (superfine), gel filtration chromatography, and reversed phase chromatography on HPLC. A homogeneous protein of molecular mass 12 kDa, as judged by silver stain, was obtained. The purification profile of the CALMP was followed in each step by its ability to stimulate bovine brain phosphodiesterase activity analogous to eucaryotic calmodulin. The amino terminal amino acid sequence (AAMKPRTGDGPLEATKEG) and two internal peptide sequences (VPLEGGGR and LVVELTPDEAAALGDELKGV) were generated by Edman degradation. Degenerate oligonucleotides were designed for 8 aminoacids from each sequence and synthesized. PCR amplification of chromosomal DNA with the oligonucleotides yielded a DNA fragment of 100 base pair size whose sequence matched with the triplet code of amino terminal DGPLEATKEG residues. The oligonucleotide for these 10 aminoacids was labeled with γ-^{32}P ATP and used as a probe in Southern hybridization. The 3000 basepair DNA band corresponding to a positive signal was excised from agarose gel, cloned into pBR322 plasmid vector, and colony hybridization was performed to identify a positive clone.

During the FY95, this positive clone will be used as a DNA probe for cloning the gene from *Mycobacterium tuberculosis* H37Rv, the etiologic agent of tuberculosis, in order to characterize the antitubercular activity of the drug trifluoperazine.

7. Purification of Proteins by Electrochromatography

H. Cabezas and K.D. Cole

Electrochromatography is being studied as a potentially efficient and scalable method for achieving high quality separation of proteins from protein mixtures. The typical set-up for electrochromatographic separations is a chromatographic column in which an electrical field is present. We have studied this process using both experimental and theoretical tools. Several columns of different designs have been constructed. The operating characteristics of each have been investigated with model protein systems. The model protein systems include mixtures of bovine serum albumin, myoglobin, and β-lactoglobulin A and B. We have investigated different chromatography media. We find that the separation of any two solutes depends upon their relative electrophoretic mobilities, on their dispersion on the column, and most importantly on their electrically induced retention in the column. The electrically induced retention of proteins acts as a multiplier of differences in electrophoretic mobilities of solutes. The electrical conductivity of the packed bed has been investigated. Measurements on Sephadex resins indicate that they have a fraction of the conductivity of the surrounding buffer solution. These results have significant implications for the underlying physical mechanism in electrochromatography. We have constructed a mathematical model which is capable of predicting the elution time and peak width of the solutes with reasonable accuracy. This model includes scaling expressions for the effect of dispersion, electrical field, flow rate, and other variables. Using results from our theoretical and experimental work we have shown the effect on the separation of varying ionic strength, pH, column length, bead size and porosity, electric field, and flow rate. We are currently studying the use of electrochromatography to separate other biological polymers.

8. Multi-dimensional NMR Spectroscopy of Bacterial Oligosaccharides and Polysaccharides

B. Coxon, V. Poszgay (National Institute of Child Health and Human Development) and P. Kovac, L. Mulard, and C.P.J. Glaudemans (National Institute of Diabetes and Digestive and Kidney Diseases)

As part of a project sponsored by the National Institutes of Health, a large series of synthetic oligosaccharide fragments of the capsular lipopolysaccharide of Shigella dysenteriae type 1 is being studied by a variety of multi-dimensional NMR techniques at 400, 500, and 600 MHz, including the selective 1D TOCSY, 2D TOCSY, 2D COSY, NOESY, HETCOR, J-resolved, HMQC, and 3D TOCSY-NOESY methods. The objective of these studies is to determine the structures and conformations of these derivatives, and to relate these properties to the antigenic activity of the compounds by binding studies (at the NIH) with monoclonal antibodies raised against the Shigella organism. One particular goal is to define oligosaccharide fragments that express conformational features of the O-specific polysaccharide, to provide a rational basis for vaccine design. In our recent work, a hexasaccharide has been studied by homonuclear, 3D TOCSY-NOESY NMR, thus providing a method for circumventing inefficient TOCSY magnetization transfers through small, scalar coupling constants in galactose residues, by continuing the transfer from H-4 to H-5 by through-space NOESY interaction. This enhances the methods available for generating proton NMR spectral assignments. The structure and ring conformations of an octasaccharide that contains two complete repeating units of the polysaccharide have also been determined. In future work, a new series of deoxy and fluorinated oligosaccharides will be studied, as part of an effort to define the precise antibody binding sites in the galactose subunits of the oligosaccharide.

9. Electron Transfer Between Metalloproteins and Electrodes

A. Gaigalas, G. Niaura (George Washington University), V. Reipa (UCLA), L. Wong (UCLA), and V. Vilker

Many metalloproteins that are catalytically active, or are electron transfer partners in enzymatic transformations, have metal centers which are asymmetrically located in the apoprotein matrix. The engineering of electrodes to provide efficient electron transfer to these metal centers is greatly facilitated by learning how proteins orient at the electrode surface when electron transfer occurs. Surface Enhanced Raman Spectroscopy (SERS) has been used to study orientation of three metalloproteins. In the case of azurin adsorbed on a silver electrode, a group of new lines was observed which were assigned to vibrations involving copper and the nitrogen of an imidazole ring. The orientation of the imidazole ring is perpendicular to the electrode surface and may serve as a pathway for electron transfer from the copper atom to the electrode interface. Studies were carried out on the adsorption and redox behavior of cytochrome c adsorbed on gold electrode modified by silver atoms deposited with an underpotential. It was found that the surface coverage by the foreign adatoms exerted a strong influence on the orientation of the adsorbed proteins. SERS spectra was obtained for putidaredoxin, preadsorbed on a bare silver electrode. Preliminary analysis suggested parallel orientation of the 2Fe-2S center relative to the electrode surface and a strong interaction between the C-terminal based tryptophan and the silver surface.

Current efforts consist of SERS study of plastocyanin and azurin under varying electrode potentials, modification of electrodes for optimizing putidaredoxin electron transfer, and developing modeling capabilities for the protein-electrode system.

10. Biocatalysis in Non-Aqueous Media

R.N. Goldberg, Y.B. Tewari, P.C. Pandey (Hindu Banaras University, India), M.V. Rekharsky, and M.M. Schantz (835)

The use of biological enzymes in commercial processes such as chemical manufacturing would be greatly enhanced if non-aqueous media could be employed. The desire for non-aqueous media is driven by considerations such as the solubility of reactants and products, and also by the fact that by reducing the amount of water in the system, the position of equilibrium can be reversed from what it is in aqueous media. This opens the possibility for improved product yields, for the synthesis of substances previously available only in small amounts, and novel compounds. There is almost a total lack of thermodynamic information on these reactions in the literature. The reaction we studied as a model system was:

$$\text{N-acetyl-L-phenylalanine} + \text{ethanol} = \text{N-acetyl-L-phenylalanine ethylester} + H_2O$$

This reaction is catalyzed by α-chymotrypsin, which we immobilized on glass beads. Equilibrium constants and enthalpies of reaction were measured with carbon tetrachloride, 1-dichloromethane, toluene, and aqueous phosphate buffer as solvents for the reactants and products. In the non-aqueous media, the position of equilibrium favors the synthesis of ester. In water, the position of equilibrium is completely reversed, and N-acetyl-L-phenylalanine ethylester is hydrolyzed almost completely to N-acetyl-L-phenylalanine and ethanol. The results of this study and the very limited amount of information available from the literature are suggestive of the rule that equilibrium constants for hydrolysis reactions in different solvents are comparable if the reaction refers to neutral species and the concentration of water is included in the formulation of the equilibrium constant. The quantitative information obtained in this study, and the observations that can be generalized from it, can serve to guide synthetic efforts in this area. Future plans for research in this area include a thermodynamic study of the synthesis of n-propylgallate from n-propanol and gallic acid using the immobilized enzyme tannase.

11. Thermodynamic Database for Enzyme-Catalyzed Reactions: Transferases and Hydrolases

R.N. Goldberg and Y.B. Tewari

The use of enzyme-catalyzed reactions in commercial processes such as chemical manufacturing requires thermodynamic data that is used in process design and optimization. Thermodynamic data on enzyme-catalyzed reactions play an important role in the prediction of the extent of reaction and the position of equilibrium for any process in which these reactions occur. Because of the very limited nature of the reviews of this subject in the literature, we have continued our earlier work in this area and completed reviews on two major classes of enzymes, i.e. the transferases and the hydrolases. In these reviews, equilibrium constants and enthalpy changes for reactions catalyzed by these enzymes have been compiled. For each reaction the following information is given: the reference for the data; the reaction studied; the name of the enzyme used and its Enzyme Commission number; the method of measurement; the conditions of measurement (temperature, pH, ionic strength, and the buffer(s) and cofactor(s) used); the data and an evaluation of it; and, sometimes, commentary on the data and on any corrections which have been applied to it. The thermodynamic conventions pertinent to the tabulation of equilibrium data have been discussed. A distinction is made between those thermodynamic quantities which pertain to the overall biochemical reaction and those which pertain to a reference reaction that involves specific species. The data from 430 references have been examined and evaluated. Work is now proceeding on the completion of the thermodynamic data for the remaining classes of enzymes, i.e. the lyases, isomerases, and ligases. Following this, the entire database will be made available in a computer-based form.

12. Light Scattering Studies of Diffusion of Proteins and Liposomes in Concentrated Solutions and Near Surfaces

J.B. Hubbard, A. Gaigalas, V. Reipa (UCLA), A. Plant, and J. Edwards

The design of biochemical reactors for use in commercial processes requires data on numerous chemical and physical properties of the biological macromolecules to be employed in the processes. This project is focussed on the measurement of diffusion coefficients by dynamic light scattering, which are particularly important for understanding mixing effects under a wide range of conditions.

Dynamic light scattering experiments were performed on concentrated solutions of BSA, lysozyme, and lactoglobulin in the vicinity of their isoelectric points. The mutual or collective diffusion coefficients of these proteins were then obtained as functions of protein concentration and solution viscosity, a property which was measured independently. This information is important in characterizing limitations to protein separation efficiency and is also valuable in understanding concentration polarization effects near membranes and other surfaces. These measurements were then compared with a general theory originally developed for diffusion in binary fluid mixtures near a critical mixing point. In contrast to previous models, this theory does not require that the volume fraction of suspended or dissolved protein is a small parameter.

In another study, dynamic evanescent wave light scattering was performed on charged liposomal vesicles in the vicinity of a charged fused silica surface. The purpose of this experiment was to determine the effects of surface-induced electrostatic and hydrodynamic interactions on liposomal diffusion in a thin fluid surface layer. It was found that a simple surface-hydrodynamic interaction model provided an accurate description of diffusion if the electrostatic interaction with the charged surface was repulsive. However, anomalous collective surface dynamics appeared when the liposomes possessed a charge opposite to that of the glass surface. Future studies will include evanescent light scattering from protein solutions in the vicinity of modified electrodes and solid membranes.

13. Biocatalysis of Non-Native Substrates by Cytochrome P450

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

Major new commercial applications for oxidoreductase enzymes await if technologists can learn how to exploit the ability of these enzymes to build up more complex molecules from simpler ones, or transform existing toxic compounds into less hazardous materials. During the latter part of the fiscal year, a new research project was initiated to learn how to engineer these enzyme systems to operate efficiently and economically. Project feasibility was established by showing the conversion of tetralin, a polycyclic hydrocarbon, into a high value-added product, stereospecific 1-tetralol, by one of the family of cytochrome P450 redox enzymes. The detoxification of aqueous solutions of halocarbons was also demonstrated, and the nature of products generated shown to depend on the concentration of oxygen in the reacting mixture. Assessing the commercial potential for reactions such as these where two substrates, hydrocarbon and oxygen, react in the presence of the P450 catalyst to form one or more products, is seriously hampered by a lack of thermodynamic and kinetic data. Such data are needed to allow prediction of reaction yields and the energy costs of the process.

Research planned for the upcoming year includes using the three protein cytochrome P-450$_{cam}$ enzyme system produced in recombinant hosts to study the *in-vitro* transformations of tetralin to 1-tetralol, and 1,2-dibromo-3-chloropropane to other halocarbons in the presence of oxygen ranging from 0.01 v/v% air saturation to 100 v/v% saturation. Product distributions will be quantified using chromatographic methods, and thermochemical measurements will be made by using microcalorimetry. Equilibrium constants and enthalpies of reactions will be determined from these measurements.

14. Thermodynamics of Antigen-Antibody Binding Using Specific Anti-Lysozyme Antibodies

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Production of antibodies in the blood provides the first line of defense against the introduction of foreign bodies in the body such as viruses. Antibodies are produced to bind to the specific foreign body which is called an antigen. This leads to eventual removal of the antigen from the blood. The mechanism for antibody-antigen binding is not well understood.

Titration calorimetry measurements have been performed on the binding of lysozyme antigen to five IgG antibodies and to fragments of the antibodies where the binding occurs. The antibodies isolated from the blood plasma of mice after a primary and secondary response upon an injection of lysozyme.

It had been assumed that this protein-protein interaction occurred by "squeezing out" water from between the antigen-antibody, and thus allowing direct intermolecular interactions between the amino acid residues of both proteins. This type of interaction would result in a small amount of heat exchanged with the environment. However, the antibody-antigen interactions exhibit an enormous loss of heat upon binding. X-ray structural analysis of two of the antibody-lysozyme complexes also show that water is retained in the interface upon antibody-antigen binding. Thus, water is intimately involved in the binding by forming a hydrogen bridged network between the two proteins. This would account for the large heat loss.

It was also found that the binding thermodynamics between the antibody and antigen is the same for the whole antibody as for the fragment of the antibody where the binding occurs. Since these fragments can be generated using molecular biology techniques on *E. coli* bacteria, fragments can be produced which mimic the highly specific binding properties of the whole antibody. Titration calorimetry measurements are presently in progress on these E coli bacteria expressed fragments where single amino acid residues have been replaced at the binding interface. Changes in the lysozyme binding thermodynamic parameters determined from these measurements will be used, along with the X-ray crystallographic determined structures of the lysozyme-mutated fragment complexes, to relate the parameters to interactions on the molecular level between the antigen and antibody.

15. Aspects of the Mechanism of Phosphate Ester Hydrolysis by Ribonuclease A

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

The use of protein engineering to adapt biological enzymes for non-biological applications such as chemical manufacturing requires the development of predictive models that relate protein structure to function. A major obstacle to this model development is the use of computational chemistry methods to describe chemical reactions for molecules as large as enzymes. Ribonuclease is a digestive enzyme whose function is to hydrolyze strands of RNA. Bovine pancreatic ribonuclease A (RNase A) is one of the most studied enzymes from a structural point of view. Crystallographic structures, with and without inhibitors bound, have been determined to nearly 0.1 nm resolution. Thus, RNase A is an ideal model for testing computational methods for studying enzyme mechanisms. Although it has been well characterized, there are many detailed issues about the mechanism which remain unresolved. In this study, a model transphosphorylation reaction has been studied using theoretical *ab initio* electronic structure methods which incorporate, for the first time, detailed all-electron components that mimic residues within the RNase A active site. Structures and relative energetics of species leading to intermediate phosphorane formation have been determined. A low energy pathway for transphosphorylation was identified which incorporates key components found in the active site including a general acid to maintain neutrality of the system, and an acid/base pair which cooperatively facilitates proton transfer. This implies that, in the presence of the right minimum environment for a specific reaction pathway, the *intrinsic* barrier to transphosphorylation is low. The results also have important mechanistic implications for RNase A, and suggest a specific role for each of the three important active site residues (His 12, His119, and Lys 41). Future studies will incorporate new theoretical methods for including in the calculations discrete water molecules and major portions of the enzyme active site, in order to understand the effects of structural constraints and electrostatic interactions on the mechanism.

16. Structure and Function of the Xenobiotic Substrate Binding Site of a Glutathione S-Transferase as Revealed by X-ray Crystallographic Analysis of Product Complexes with the Diastereomers of 9-(S-Glutathionyl)-10-hydroxy-9,10-dihydrophenanthrene

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The glutathione S-transferases are a group of enzymes that catalyze the nucleophilic addition of the tripeptide glutathione to substrates bearing electrophilic functional groups. As such, they are probably the single most important class of enzymes involved in the detoxification of endogenous and xenobiotic electrophilic substrates. These enzymes are ubiquitous and abundant in mammalian tissues and have been found to play a central role in the detoxification of carcinogens as well as anticancer therapeutic agents.

The three-dimensional structures of two product complexes of isoenzyme 3-3 of recombinant rat liver mu class glutathione S-transferase have been determined to high resolution by x-ray crystallographic techniques. The products were synthesized by the addition of glutathione to phenanthrene 9, 10-oxide. These complexes reveal that the xenobiotic substrate binding site is a hydrophobic pocket lined by residues near the N-terminus in the N-terminal glutathione binding domain, and two regions of the C-terminal domain. The position of the glutathione is similar to that found in our previously reported studies. In these studies the difference between the interactions of tyrosine 115 with the diastereomer products led to further investigation involving site-directed mutagenesis of the tyrosine to phenylalanine. Characterization of this mutant indicated that tyrosine 115 was implicated in catalysis, but only for particular classes of substrates.

This work contributed to the remarkable discovery that for glutathione S-transferase, different amino acid residues of the protein are involved in catalysis depending upon what class of substrate is bound to the surface of the protein.

17. *In vivo* Assembly of Rhodopsin-like Complexes from Independently Expressed Polypeptide Fragments

K.D. Ridge, S. Lee (CARB/UMD), and L. Yao (University of Virginia)

The structure and folding properties of membrane-bound proteins is poorly understood and yet is critical to our understanding and eventual control of important classes of proteins that include ion channels, cellulon recognition sites, and signal transducers. Detailed knowledge of membrane proteins would be useful in pharmaceutical design, biosensor development, and molecular materials development.

The rod cell photoreceptor rhodopsin is a prototypical member of the superfamily of guanine nucleotide-binding protein (G protein) coupled receptors which regulate a variety of sensory, hormonal, and neural responses. Bovine rhodopsin is composed of the apoprotein opsin, a single polypeptide chain of 348 amino acids which traverses the membrane lipid bilayer seven times, and an 11-*cis*-retinal chromophore which is covalently linked to the protein via a Schiff base. Although knowledge of the static rhodopsin structure has yielded to investigation, the dynamic aspects of rhodopsin conformation such as folding and assembly *in vivo* and *in vitro* have eluded a detailed understanding at the molecular level.

The folding and assembly of opsin has been investigated by the expression of opsin gene fragments separated at points corresponding to proteolytic cleavage sites. Five different opsin polypeptide fragments were stably produced upon expression of the corresponding genes in eukaryotic cells. The individually expressed opsin polypeptide fragments failed to form the rhodopsin chromophore with 11-*cis*-retinal. However, rhodopsins with spectral characteristics similar to the native visual pigment were successfully formed by co-expression of two or three complementary polypeptide fragments. One of these rhodopsins showed substantial light-dependent activation of the retinal G protein. Therefore, the functional assembly of bovine rhodopsin does not require covalent linkage of the polypeptide chain and may be mediated by the stable association of multiple protein-folding domains.

Further efforts are aimed at identifying additional sites in the opsin polypeptide chain which permit polypeptide fragment assembly and establishing whether these opsin polypeptide fragments do indeed represent one or more protein-folding domains.

18. The Biological Macromolecule Crystallization Database, Version 3.0: New Features, Data, and the NASA Archive for Protein Crystal Growth Data.

G.L. Gilliland, M.Tung, D.M. Bickham (SRDP), and J. Ladner

X-ray crystallography is the most widely-used method for determining protein structures which are used in pharmaceutical design, materials development, and structure/function research. Crystallization of proteins and other biological macromolecules remains a poorly understood phenomenon, and yet is critical to the determination of structure. The NIST/NASA/CARB Biological Macromolecule Crystallization Database (BMCD) is used by scientists to reproduce known crystallization conditions and to develop strategies for the crystallization of new proteins.

Version 3.0 of the NIST/NASA/CARB Biological Macromolecule Crystallization Database (BMCD) includes crystal and crystallization data on all forms of biological macromolecules which have produced crystals suitable for x-ray diffraction studies. The data includes summary information on each of the macromolecules, crystal data, crystallization conditions, and comments about the crystallization procedure if it varies from the traditional methods employed for crystal growth. The database management software maintains continuity with previous versions providing similar search procedures and displays. Version 3.0 of the BMCD includes protocols and results for crystallization experiments undertaken in space. This new data is comprised of both the NASA Protein Crystal Growth Archive, which includes information on all NASA sponsored protein crystal growth experiments and data describing other internationally sponsored microgravity macromolecule crystallization studies. The entries for the space growth crystallization experiments contain the crystallization protocols, apparatus descriptions, flight summary data, indication of success or failure of the experiments, references, etc. Other new features of the BMCD include the addition of crystallization procedures for small peptides and cross references to other structural biology databases.

19. The Structure of Subtilisin BPN'at 1.6Å Resolution and Comparison of Three High-Resolution Crystal Forms

T. Gallagher, J. Oliver (Procter and Gamble Company), R. Bott (Genencor International, Inc.), C. Betzel (European Molecular Biology Laboratory, Hamburg, Germany), and G.L. Gilliland

Subtilisin BPN' is an industrial enzyme (used in detergents) that is also of widespread scientific interest for its stability, folding, and crystallization properties. We have refined its atomic structure at high resolution (the highest ever published) based on X-ray diffraction data from crystals belonging to space group C2. We have analyzed the new structure and compared it with previous structures in two other space groups.

Two key features examined are the active site and the crystal packing interactions. The resolution is so high and the data of sufficient quality that several conformations of key active site residues can be seen. The importance of crystallization to protein structure determination has prompted us to compare the packing in three crystal forms. One conclusion is that the arrangement of the water that binds to the protein in solution determines the geometry of the contacts that lead to crystal growth.

This enzyme is the subject of active research both at NIST and elsewhere, with the goal of engineering it for greater stability and for variations in its protease activity. Two of our collaborators represent companies (Joel Oliver of Procter and Gamble; Richard Bott of Genencor International) that are also involved in these efforts. Thus the present work is expected to lead to improvements in detergent technology, as well as advances in scientific understanding of enzymes. Efforts in FY95 involve several stabilized variants and a new crystal form of subtilisin. These are being investigated for their catalytic activity and 3-dimensional structure.

20. Non-Specific Binding in Alkanethiol-Coated Gold Surfaces

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

The nonspecific binding (NSB) of proteins to surfaces results in lowered signal-to-noise ratios in biosensor devices which interact with biomolecules. We are studying NSB in order to understand the mechanisms by which it occurs. Such knowledge will allow us to develop technologies to eliminate or reduce NSB, and thus increase the sensitivity and specificity of biosensors. This work is sponsored by the Consortium on Advanced Biosensors (CAB), a group of industrial companies interested in manufacturing and selling biosensors in the clinical, environmental, and bioprocessing markets around the world.

We are studying protein adsorption to well-defined surfaces consisting of self-assembled molecular monolayers (SAMs). The SAMs are crystalline-like monolayers that form spontaneously when a clean gold surface is immersed in an ethanolic solution containing an alkanethiol ($HS(CH_2)_nR$). We have used C_{11} and C_{16} thiols terminated with various functional groups. These surfaces were characterized using ellipsometry and contact angle goniometry to measure film thicknesses and surface wettability, respectively.

We have examined the adsorption of the proteins bovine serum albumin (BSA), and immunoglobulin G (IgG) to SAM surfaces using ellipsometry, fourier transform infrared reflection spectroscopy (FT-IR), surface enhanced Raman spectroscopy (SERS), and surface plasmon (SP) techniques. Ellipsometry was used to measure effective protein thicknesses; FT-IR and SERS were used to study protein conformational state and orientation; and SP was used to study the kinetics of protein adsorption to SAM surfaces. All studies, except for the SP experiments, were carried out *ex-situ* using protein films dried after their deposition from buffered solution. The SP experiments were carried out *in-situ*.

We have studied -OH, -COOH, and $-CH_3$ terminated alkanethiols to determine the relative binding of BSA and IgG to these surfaces. We have also compared addition of protein solution to wetted SAM surfaces versus the same solution added to a dry SAM surface. The FT-IR studies showed BSA to have mostly random coil structure (denatured structure) on all surfaces examined, while IgG had predominantly native secondary structure. SP data was used to calculate apparent equilibrium constants using a simple adsorption-desorption model. In addition, SERS experiments have indicated that BSA can be oriented on N-acetyl-L-cysteine SAMs (deposited on a silver electrode) by an applied electrical potential.

Future plans include examination of the binding characteristics of BSA and IgG on additional surfaces, each covered with ethylene glycol, phenol or maltose. These studies will complete the initial portion of this project. The next phase will involve adsorption studies on the surfaces previously showing the lowest NSG with protein conjugates of IgG.

21. Self-Assembled Lipid Bilayers on Gold Electrodes for Biomimetic Applications

A. Plant, M. Lewis, M. Guegetchkeri (Tbilisi State University, Tbilisi, Georgia), D. O'Shannessy (SmithKline Beecham Pharmaceuticals)

Phospholipid molecules are the primary components of cellular membranes, and planar phospholipid bilayer membranes are model systems for the study of cell membrane dynamics, cell membrane transporter phenomena, and receptor-specific cell membrane signal transduction. The recognition and signal transduction processes which are so important in cell physiology may also have important applications in biosensors.

To design a planar biomimetic membrane which has practical applicability as a sensor component, we have developed a method of forming phospholipid/alkanethiol hybrid bilayer membranes (HBMs) on gold electrodes. Self-assembled monolayers (SAMs) of alkanethiol provide a hydrophobic substrate for the spontaneous self-assembly of a second layer of phospholipid. The HBMs are easy to form, are stable for long periods of time, and demonstrate biomimetic characteristics.

We have been studying HBMs by electrochemistry, surface enhanced Raman spectroscopy (SERS), and surface plasmon resonance (SPR) spectroscopy. The insulating characteristics and thickness of the bilayers are consistent with the structural characteristics of natural and artificial bilayer membranes. The insulating properties respond to temperature-induced lipid phase transitions, the association of divalent cations with the phospholipid polar headgroups, and the insertion of anesthetics. The effect that the bee venom peptide toxin, melittin, has on the rate of electron transfer through the bilayer suggests that, as in natural membranes, melittin interacts with these bilayers to form protein pores. SERS provides corroborative evidence for the location of melittin, and also indicates that structural changes occur in the thiol alkane chains when the HBM is formed. Both SERS and SPR data indicate that HBMs provide effective matrices for directing biochemical interactions based on molecular specificity. HBMs are also efficient at blocking nonspecific adsorption of proteins and denaturation of immobilized proteins.

The ease of assembly, the ruggedness, and the responsiveness of HBMs suggest that they will be very suitable for development as sensors for anesthetics, ions, and membrane protein-specific function.

22. Genetically Engineered Self-Assembling Pores for Biosensor Applications

J.J. Kasianowicz and B. Robertson

With the goal of producing rationally designed components of biosensors that have a wide spectrum of sensitivities and selectivities for a variety of water-soluble ligands, we are characterizing proteins that self-assemble to form well-defined nanoscale pores, or ion channels, in lipid bilayer membranes. The concentration of ligand will be determined by its affinity for binding sites that are genetically engineered to be located inside the pore. Ligands binding to these sites block the pore, leading to a reduction in the ionic current. The mean and variance of the current are used to estimate the equilibrium constant of the reaction. Spectral analysis of single channel current fluctuations could ultimately be used to determine the kinetic rate constants.

In collaboration with H. Bayley (Worcester Foundation for Experimental Biology) we are currently developing genetically engineered versions of the well defined α-hemolysin protein from *Staphylococcus aureus* for use in detecting, with high selectivity and specificity, heavy metal transition cations. The α-hemolysin pore has several properties that make it particularly attractive for use in biosensors. It self-assembles to form pores that are large enough (inner diameter 1.1 - 2.5 nm) that various functional groups can be incorporated in front of or inside the pore by targeted chemical modification. However, the pore is sufficiently small that the ion conduction pathway will be blocked by a single ligand, thus creating a large change in ionic current. Lastly, the primary sequence contains no cysteines. Thus introducing a cysteine into the sequence produces a unique site to which specific binding sites can be chemically linked.

We recently found a region near the midpoint of the polypeptide that is in the pore. Sensitivity to Zn^{2+} was conferred to the channel by replacing 5 consecutive residues in this region with histidines (the imidazole rings of spatially adjacent histidines coordinate metal cations). We are currently characterizing point mutants in this region to further determine which residues line the interior of the pore. In addition to the potential application to biosensor technology, this method should allow us to determine the channel's topology.

23. Competitive DNA Intercalation

J. Horvath, P. Pandey (Baranas Hindu University, Varanasi, India), and H.H. Weetall

We have shown that fluorescent dyes intercalated in double-stranded DNA can be displaced by the addition of polyaromatic hydrocarbons (PAH) having two or more adjacent rings. This provides the basis for the development of a novel class of biosensors for the detection of PAH in the environment.

Double-stranded DNA has been entrapped on the surface of a fiber using acrylamide-methacrylamide-hydrazide prepolymer. The response of the double stranded DNA fiber to ethidium bromide using evanescent wave total internal fluorescence spectroscopy was significantly high compared to the response obtained with unmodified fibers. The high response is due to the intercalation of the dye within the DNA, giving rise to enhanced interaction of evanescent energy with the fluorophore. The detection of aromatic compounds was based on the differential affinities of these molecules for the DNA. There was a decrease in steady-state response, obtained at constant concentration of the dye, upon injection of the PAH. The sensitivity of the system is presently in the ppm to ppb range.

A series of 15 carcinogenic and non-carcinogenic PAHs were studied by DNA intercalation-fluorescence polarization, using acridine orange as the intercalating fluorescent dye for quantitative measurements. The polarization value of the DNA/acridine complex decreases with addition of various concentrations of test molecules. No systematic relationship between carcinogenicity and intercalation sensitivity (limits of detection) were observed. Measurements comparing calf thymus and *E. coli* DNAs for intercalation, indicated that the use of synthetic DNAs of different base pair combinations should yield better sensitivities and improved selectivity. Future experiments will examine SRMs of typical environmental samples such as Diesel Particulate Matter (SRM 1650) and Urban Dust/Organics (SRM 1649), and different oligonucleotide sequences for improved detection limits. This technique may lead to portable sensing device for *in-situ* environmental monitoring.

24. Electro-optical Properties of Bacteriorhodopsin on Semi-Conducting Electrodes

B. Robertson and E. P. Lukashov (Moscow State University, Moscow, Russia)

Bacteriorhodopsin (bR) is a protein isolated from the purple patches of the halophilic bacterium *Halobacterium salinarium*. This light-sensitive protein has optical and electrical properties that make it potentially valuable as a material source for information storage and retrieval. In addition, this material may find application in gating, switching, and as an artificial retina in robotics devices. Studies have been carried out in an effort to better understand the electro-optical properties of bR. Films of purple-membrane patches containing bacteriorhodopsin (bR) were deposited on various electrode materials and studied electrochemically. When activated by yellow light, bR pumps protons across the membrane. With the film in contact with the electrode surface, the protons change the pH at the electrode surface and thereby generate a transient electrochemical current. This provides a measurement of the rapid pH change, which has been calibrated and found to be highly sensitive.

A transparent electrode with a tin-oxide coating on glass was used for the initial studies. The tin oxide participates in the reaction and provides the sensitivity to the pH change. At present, a gold electrode insulated with a self-assembled alkylthiol monolayer is being studied. In this case, dissolved oxygen provides the sensitivity to the pH change. In both cases the photocurrent is a reflection of the properties of bR.

It may be possible to perturb the photocycle of bR by some form of ligand binding reaction on the surface of the film, using antigens and antibodies. We are exploring the possibility that this binding reaction will be detectable by a change in the transient photocurrent. In addition we plan to acquire commercially available chips containing multi-pixels for further investigation of the possibilities of using the bR in an artificial retina.

25. Modification of Enzyme Kinetics by Light-Driven Proton Pumping

M.F. McCurley and S.A. Glazier

A novel method is being investigated to optically modulate enzyme activity by modulating pH. Bacteriorhodopsin (bR) is a trans-membrane protein found in *Halobacterium salinarium* that is receiving considerable attention in research laboratories for possible use in biosensors and molecular electronic devices. The bR protein (MW 26 KDa) contains a retinal chromophore that gives it a characteristic purple color. The conformation of bR consists of 7 α-helices that surround the retinal chromophore. Five of the seven α-helices of the bR contribute 26 amino acids to form a proton channel in the protein. When illuminated, bR undergoes a photocycle consisting of several intermediate states that have different spectral properties. During the photocycle, protons are pumped through the proton channel from one side of the membrane to the other.

In this study, the proton pumping activity of bR was used to control the conversion of sucrose to glucose by the pH-sensitive enzyme, invertase. bR was oriented within the lipid bilayer of phosphatidylcholine vesicles. When the pH of the solution surrounding the vesicles was greater than 4, bR pumped protons from the bulk into the aqueous interior of the vesicles when illuminated at the appropriate wavelength. At a bulk solution pH of less than 3, light caused a net flow of protons into the bulk. This response caused small, but significant pH changes in the bulk solution, which resulted in detectable quantitative changes in the enzyme kinetics. We believe that under the proper conditions it should be possible to turn an enzyme on and off in this manner.

26. Development of a Sensor for Nitric Oxide

S.A. Glazier and G. Gabor (Israel Institute for Biological Research, Ness-Zion, Israel)

The importance of nitric oxide (NO) in mammalian systems has recently been established. Nitric oxide plays several roles within these systems. First, it is believed to be the endothelium-derived relaxing factor (EDRF) which causes relaxation of vascular smooth muscle and ultimately blood pressure reduction. Second, it can be synthesized by macrophage cells as a toxin in response to the presence of cytokines from tumor and invading parasite cells. Third, nitric oxide is thought to inhibit platelet aggregation and adhesion to blood vessels thus decreasing blood's ability to clot. Last, it appears to act as a neurotransmitter when generated by nerve cells. It is possible that nitric oxide plays additional roles in mammalian systems which are yet to be discovered.

Work is underway to construct sensors for nitric oxide which will be as selective in their measurement as possible while meeting the requirement of operation in the 1 μM to 1 nM concentration range of nitric oxide. To this end, sensors based on nitric oxide scavenging by oxyhemoglobin are being prepared. In these sensors, the spectral absorption of hemoglobin shifts as oxyhemoglobin is converted to methemoglobin. The mechanism involves the conversion of the oxygen in the oxyhemoglobin to a superoxide which binds the NO, forming a peroxynitrate which quickly decays to nitrate. This mechanism, followed by spectral changes can quantitate the NO present in the oxyhemoglobin solution. In another sensor, nitric oxide is scavenged by thiol-containing compounds to form nitrosothiols. These nitrosothiols then modulate the fluorescence of fluorophores by quenching. In this way, nitric oxide concentration can be related to changes in fluorescence signals.

It is envisioned that additional sensors based on oxyhemoglobin/fluorophore effects may be possible, on inhibition of the enzyme, aconitase, and on electrochemical reduction of methemoglobin formed in the oxidation of oxyhemoglobin by nitric oxide. We are pursuing collaborations which will allow us to test our sensors in a number of biological systems.

C. Outputs and Interactions (Biotechnology Division)

1. Publications

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2. Talks

Ashton, R., "Protein Interactions in Biosensor Applications," Abiomed, Inc., Danvers, MA, October 31, 1993.

Ashton, R., "Preparation of Anhydrothrombin," Meeting of American Society for Biochemistry and Molecular Biology, Washington, DC, May 25, 1994.

Atha, D.H., "Physical Characterization of Heparin by Light Scattering," Second Annual Conference on Glycotechnology, La Jolla, CA, May 16, 1994.

Cabezas, H. and Cole, K., "Electrochromatographic Purification of Proteins," 207th American Society National Meeting, San Diego, CA, March 15, 1994.

Cabezas, H. and Cole, K., "Protein Separation by Electrochromatography: Theory and Experiment," 13th Southern Biomedical Engineering Conference, Rockville, MD, April 17, 1994.

Cabezas, H., Cole, K., and Lerman, J., "Electrochromatographic Purification of Proteins," Workshop on Chromatography, Electrokinetics, and Separations in Porous Media, NIST, Gaithersburg, MD, August 4, 1994.

Cole, K. and Cabezas, H., "Electrochromatography: Experimental Results and Matehematical Modeling," National Meeting of the Electrophoresis Society, Charleston, SC, November 7, 1993.

Cole, K., "Use of Electrochromatography for Protein Separations," Center for Separation Science, Department of Chemical Engineering, University of Arizona, Tucson, AZ, November 29, 1993.

Cole, K., "Overview of Biotechnology Research at NIST," Biotechnology and Mimolecular Sciences Colloquium at Pacific Northwest Laboratory, Richland, WA, March 16, 1994.

Coxon, B., "NMR Studies of Oligosaccharides That Can Recognize an Anti-Shigella dysenteriae Type 1 Antibody," 1993 Bruker NMR Users Conference, Westford, MA, October 6, 1993. Invited

Coxon, B., "Application of One- and Two-Dimensional TOCSY NMR Methods to Structural nalysis of Biomolecules," Department of Chemistry, the American University, Washington, DC, April 6, 1994. Invited

Coxon, B. and Pozsgay, V., "Synthesis and NMR Spectroscopy of Oligosaccharides Related to the Lipopolysaccharide of Shigella Dysenteriae Type 1," XVIIth International Carbohydrate Symposium, Ottawa, Canada, July 21, 1994.

Dizdaroglu, M.M., "Oxidative and Radiation Damage to DNA," The Ancient DNA Conference, Smithsonian Institution, Washington, DC, October 7, 1993. Invited

Dizdaroglu, M.M., "DNA Damage and Repair," Bilkent University, Ankara, Turkey, November 4, 1993. Invited

Dizdaroglu, M.M., "Oxidative and Free Radical-Induced Damage to DNA,"Conference on Oxidative Stress and Human Diseases, University of Ankara, Medical School, Ankara, Turkey, November 5, 1993. Invited

Dizdaroglu, M.M., "Determination of DNA Damage and Repair," 42nd Annual Meeting of the Radiation Research Society, Nashville, TN, May 3, 1994. Invited

Dizdaroglu, M.M., "Radiation-Induced DNA Lesions in Mammalian Cells," Department of Energy Radiological and Chemical Physics Contractors Meeting, New Orleans, LA, June 8, 1994. Invited

Dizdaroglu, M.M., "DNA Damage in Mammalian Cells," Gordon Research Conference on Radiation Chemistry, Salva Regina, RI, July 18, 1994. Invited

Dizdaroglu, M.M., "Chemistry of Free Radical Damage to DNA and Nucleoprotein," First International Meeting on Pharmacy and Pharmaceutical Sciences, Istanbul, Turkey, September 5, 1994. Invited

Dizdaroglu, M.M., "DNA Damage by Free Radicals," 4th International Marmara Medical Days, Marmara University Medical School, Istanbul, Turkey, September 7, 1994. Invited

Gaigalas, A., "Application of Dynamic Light Scattering to the Characterization of Collagen Molecules," Collagen Corp., Palo Alto, CA, March 1, 1994.

Gaigalas, A., "Application of Evanescent Wave Scattering to the Study of the Motion of Liposomes Near an Interface," 13th Southern Biomedical Engineering Conference, Rockville, MD, April 16, 1994.

Gallagher, T., "Design of a New Biomolecular Docking Interactive Exhibit for the Smithsonian Museum of American History," NIST Alumni Meeting, January 13, 1994. Invited

Gallagher, T., "The Structure of Subtilisin BPN' at 1.6Å Resolution: Analysis of Solvent Structure and Crystal Packing Interactions," American Crystallographic Association 1994 Annual Meeting, Atlanta, GA, June 28, 1994.

Gilliland, G.L., "The Active Site of Ribonuclease A: an Example of Solvent Modulated Specificity," Washington Crystal Colloquium, Geophysical Laboratory, Washington, DC, October 29, 1993. Invited

Gilliland, G.L., "Crystallographic Studies of the Substrate Specificity and Mechanism of Class Mu Glutathione S-Transferase," University of Alabama, Huntsville, AL, January 14, 1994. Invited

Gilliland, G.L., "The Three-Dimensional Structure of Glutathione S-Transferase: Crystallographic Analysis of Catalysis and Substrate Specificity," Biochemistry Department, University of Maryland School of Medicine, Baltimore, MD, January 31, 1994. Invited

Gilliland, G.L., "The Three-Dimensional Structure of Glutathione S-Transferase: Crystallographic Analysis of Catalysis and Substrate Specificity," Biochemistry Department, School of Medicine, Vanderbilt University, Nashville, TN, May 16, 1994. Invited

Gilliland, G.L., "Difficult MIR Structure Determinations: Glutathione S-Transferase, A Case Study," Workshop on Isomorphous Replacement Methods in Macromolecular Crystallography at The American Crystallography Association Annual Meeting, Atlanta, GA, June 25, 1994. Invited

Gilliland, G.L., "Glutathione S-Transferase: Site-Directed Mutagenesis and X-ray Crystallographic Studies of Catalysis and Substrate Specificity," 23rd Linderstrom-Lang & 4th INPEC Conference on Protein Engineering, Aarhus, Denmark, July 5, 1994. Invited

Gilliland, G.L., "The Three-Dimensional Structure of Glutathione S-Transferase: Crystallographic Analysis of Catalysis and Substrate Specificity," University of Lund, Lund, Sweden, July 7, 1994. Invited

Gilliland, G.L., "Crystallographic and Structural Analysis Studies of Recombinant and Chemically Modified Hemoglobins Designed to Aid Development of Artificial Hemoglobin-Based Oxygen Carriers," XI Congress of the International Society for Artificial Cells, Blood Substitutes, and Immobilization Technology, Boston, MA, July 25, 1994. Invited

Glazier, S., "Response of a Novel Rhodopsin Based Fiber Optic Sensor to Organic Solvents," 3rd World Congress on Biosensors, New Orleans, LA, June 3, 1994.

Goldberg, R., "Thermodynamic Data for Bioprocess Engineering," AIchE 1993 Annual Meeting, St., Louis, MO, November 8, 1993.

Goldberg, R., "Thermodynamics of the Hydrolysis of L-Tryptophan to (Indole + Pyruvate + Ammonia)," NIST, Gaithersburg, MD, November 30, 1993.

Goldberg, R., "Thermodynamics of Enzyme-Catalyzed Reactions: Transferases," 13th IUPAC Conference on Chemical Thermodynamics, Clermont-Ferrand, France, July 19, 1994.

Goldberg, R., "Thermodynamics of the Hydrolysis of N-acetyl L-phenylalanine Ethyl Ester in Water and in Non-aqueous Solvents," 49th Calorimetry Conference, Santa Fe, NM, August 1, 1994.

Goldberg, R., "Thermodynamics of Enzyme-Catalyzed Reactions: Transferases," 49th Annual Calorimetry Conference, Santa Fe, NM, August 2, 1994.

Goldberg, R., "Thermodynamic Data For Bioprocess Engineering," American Chemical Society National Meeting, Washington, DC, August 21, 1994.

Grayson, D. and Vilker, V., "Synthesis of Added-Value Products Using the Reconstituted P-450$_{\text{cam}}$ Enzyme System," Annual American Institute of Chemical Engineers Meeting, St. Louis, MO, November 9, 1993.

Horvath, J., "Detection of Carcinogens via DNA Intercalation and Evanescent Wave Fiber Optic Fluorimeter," 3rd World Congress on Biosensors, New Orleans, LA, June 3, 1994 (presented by S. Glazier).

Kasianowicz, J., "Ion Channels as Components of Biosensors," Sandoz Pharmaceuticals, Vienna, Austria, October 7, 1993. Invited

Kasianowicz, J., "Towards a Structure-Function Relationship for the Staphylococcus aureus," α-Toxin Channel," University of Würtzburg, Würtzburg, Germany, October 22, 1993. Invited

Kasianowicz, J., "Membrane-Bound Proteins: Their Role in Cell-Cell Communication and Survival of Organisms," Montgomery Blair HS Science Magnet program, Silver Spring, MD, November 4, 1993.

Kasianowicz, J., "Ion Channels: Role in Cell Function, Cell Damage and Biotechnology," Graduate Biotechnology course, Johns Hopkins University, Rockville, MD, November 17, 1993.

Kasianowicz, J., Walker, B., Krishnasastry, M. and Bayley, H., "Genetically Engineered Pore as a Metal Ion Biosensor," Materials Research Society Meeting, Boston, MA, December 1, 1993.

Kasianowicz, J., "Novel Physical Methods to Determine the Structure of Some Pore-forming Proteins," Department of Physics and Engineering, Eastern Nazarene College, Wollaston, MA, December 2, 1993.

Kasianowicz, J., "Membrane Proteins: Tools for Basic Research and Biotechnology," Governor's Academy for MD HS teachers, NIST, Gaithersburg, MD, January 12, 1994.

Kasianowicz, J., "Protein Ion Channels as the Basis of Neural Activity and for Technological Applications," Montgomery Blair HS Science Magnet Program, Silver Spring, MD, February 10, 1994.

Kasianowicz, J., Brutyan, R., Vodyanoy, I. and Bezrukov, S., "Noise Induced by Differently Sized Polyethylene-Glycols Shows Interaction of Polymer with the α-toxin Ion Channel," Biophysical Society Meeting, New Orleans, LA, March 10, 1994.

Kasianowicz, J., "Voltage-Dependent Gating Kinetics of an Ion Channel Modulated by Ionic Strength," Biophysical Society Meeting, New Orleans, LA, March 10, 1994.

Kasianowicz, J., "Genetically Engineered Pores," Graduate Biotechnology Course, Johns Hopkins University, Rockville, MD, April 11, 1994.

Kasianowicz, J., "Ion Binding Characterization of Mutant and Wild-Type Alpha-Toxin Channels: Implications for Biosensor Development," Gillette Research, Gaithersburg, MD, April 13, 1994. Invited

Kline, M.C., "Electrophoretic Methods for the Separation of Anodal/Cathodal Allelic Variants in Mixed Sample Lanes," The Electrophoresis Meeting, Charleston, SC, November 6, 1993.

Kline, M.C., "Interlaboratory Studies to Develop PCR-Based Reference Materials for Human Identity Testing with D1S80," American Academy of Forensic Sciences, San Antonio, TX, February 13, 1994.

Krauss, M., "Electronic Structure of the Excited States and Phenol Fluorescence," Conference on Chemical Defense Research - U.S. Army, Aberdeen Proving Ground, MD, November 17, 1993.

Krauss, M., "Spectroscopy of Uracil Radicils," NIST Chemical Science Technology Laboratory Colloquium, February 9, 1994.

Krauss, M., "Spectroscopy of Uracil Radicals," Sanibel Conference, Jacksonville, FL, February 14, 1994. Invited

Krauss, M., "Effective Fragment Potentials and Spectroscopy at Enzyme Active Sites," Meeting on Computational Methods for Large Molecules, Wroclaw, Poland, June 26, 1994. Invited

Krauss, M., "Effective Fragment Potentials and Spectroscopy at Enzyme Active Sites," Structural Biochemistry Program, Frederick Supercomputing Center, Frederick, MD, August 16, 1994.

Krauss, M., "The Mechanism of Phosphate Ester Hydrolysis," Mt. Sinai Medical School, New York, NY, September 22, 1994.

Ladner, J.E., "The Biological Macromolecule Crystallization Database and NASA Archive for Protein Crystal Growth," American Crystallographic Association Meeting, Atlanta, GA, June 28, 1994.

Levin, B.C., "Science Funding and Policy," Sigma Xi Meeting, Gaithersburg, MD, October 28, 1993. Invited

Levin, B.C., "Improving Materials by Adding Toxicant Suppressants," National Research Council Meeting, Washington, DC, December 13-14, 1993. Invited

Levin, B.C., "Toxicology," American Chemical Society Meeting, Washington, DC, August 20, 1994. Invited

Levin, B.C., "A New Approach for Predicting the Toxic Potency of Complex Combustion Mixtures," American Chemical Society Meeting, Washington, DC, August 22, 1994. Invited

McCurley, M., "Light Activated Enzyme Switch," 3rd World Congress on Biosensors, New Orleans, LA, June 3, 1994.

McCurley, M., "Biotechnology Research at NIST," NAS/NRC Panel on the Federal Investment Biobased Industrial Products, at the National Academy of Sciences, Washington, DC, July 8, 1994.

McKenney, K.H., "Protein Engineering and Gene Expression," Department of Biochemistry and Molecular Biology at George Washington University, Washington, DC, February 9, 1994. Invited

McKenney, K.H., "A New Molecular Chaperone, ClpA, Functions like DnaK and DnaJ," FASEB Meeting, Saxton River, VT, June 9, 1994. Invited

Plant, A., "Phospholipid/Alkanethiol Bilayers as Biomimetric Membranes," Keystone Conference on Biology of Physicochemical Interactions at the Cell Surface, Taos, NM, February 21, 1994.

Plant, A., "Phospholipid/Alkanethiol Bilayers: A Novel Biomimetric Model Membrane," Symposium on Domains in Biological Membranes, National Institute of Health, Bethesda, MD, March 2, 1994.

Plant, A., "Planar Phospholipid Bilayer Membranes Formed from Self-Assembled Alkanethiol Monomers," Southern Biomedical Engineering Conference, Washington, DC, April 16, 1994.

Plant, A., "Phospholipid/Alkanethiol Bilayers: A Novel Biomimetric Membrane," Federation of European Biochemical Societies Special Meeting, Biological Membranes, Helsinki, Finland, June 27, 1994.

Powell, L., "Federal Biotechnology Research," US/European Communities Task Force on Biotechnology, Arlington, VA, October 18, 1993. Invited

Powell, L., "Clinton Administration Policy Directions for Biotechnology," Canadian National Biotechnology Advisory Committee, Ottawa, Canada, December 9, 1993. Invited

Powell, L., "Biotechnology Research at NIST," Wisconsin Biotechnology Association, Madison, WI, December 14, 1994. Invited

Powell, L., "Career Opportunities in Biotechnology," University of Maryland, Chemistry Department, College Park, MD, March 10, 1994. Invited

Powell, L., "Clinton Administration Policy Directions for Biotechnology," Annual California Biotechnology Conference, La Jolla, CA, April 8, 1994. Invited

Powell, L., "Biotechnology Research at NIST," Pennsylvania Biotechnology Association, Philadelphia, PA, April 27, 1994. Invited

Reddy, P., "Cloning and Sequencing of Asp.f1 Gene of A. Fumigatus," 16th International Congress of Biochemistry and Molecular Biology, Delhi, India, September 21, 1994.

Reddy, P., "Purification and Characterization of Calmodulin like Protein from Mycobacterium Smegmatis," 16th International Congress of Biochemistry and Molecular Biology, Delhi, India, September 22, 1994.

Reddy, P., "Analysis of the Regulatory and Catatylic Domains of E. Coli Adenylate Cyclose," Center for Biochemical Technology, Delhi, India, September 23, 1994. Invited

Reddy, P., "Expression of E. Coli Adenylate Cyclose, A Lethal Gene Product," Department of Biochemistry, Delhi University College of Medical Sciences, Delhi, India, September 26, 1994. Invited

Reddy, P., "Regulation of the Activity of E. Coli Adenylate Cyclose by the Phosphoeuolpyruvate-Sugar Phosphotransferase System Proteins," Department of Biochemistry, Delhi University, Delhi, India, September 27, 1994. Invited

Reeder, D.J., "DNA Technologies at NIST," Alcohol, Tobacco, and Firearms, Rockville, MD, October 13, 1993. Invited

Reeder, D.J., "Multiple Approaches to DNA Separations in Qualifying Reference Materials for DNA Fingerprinting," 20th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Detroit, MI, October 19, 1993. Invited

Reeder, D.J., "Electrophoresis Update," Presidential Talk at the 1993 Electrophoresis Society Meeting, Isle of Palms, SC, November 17, 1993. Invited

Reeder, D.J., "Where is DNA Profiling Headed?," Technology Assessment Program, National Insitutes of Justice, Washington, DC, December 3, 1993. Invited

Reeder, D.J., "Update of Reference Materials for PCR Research," Technical Working Group on DNA Analysis Methods, FBI Laboratory, Quantico, VA, January 10, 1994. Invited

Reeder, D.J., "DNA Standards," American Academy of Forensic Sciences (AAFS) Workshop, San Antonio, TX, February 14, 1994. Invited

Reeder, D.J., "A Prototype Standard for PCR-Based Technologies," American Academy of Forensic Sciences (AAFS) Workshop, San Antonio, TX, February 17, 1994.

Reeder, D.J., "DNA Profiling and NIST Standards," University of Utah, Salt Lake City, UT, February 25, 1994. Invited

Reeder, D.J., "DNA Identity Testing in Forensic Sciences," Catholic University, Washington, DC, April 15, 1994. Invited

Reeder, D.J., "Reference Materials for Standardization of DNA Typing Materials," Sixth International Symposium on Biological and Environmental Reference Materials, Kona, HI, April 18, 1994.

Reeder, D.J., "DNA Profiling," NIST Summer Symposium Series, Gaithersburg, MD, July 22, 1994. Invited

Reeder, D.J., "Update on NIST's Interlaboratory Tests of Prototype Standard for PCR Technologies," Technical Working Group on DNA Analysis Methods, FBI Laboratory, Quantico, VA, July 25, 1994. Invited

Richie, K.L., "New Probes and Chemiluminescent Methods Applied to Standard Reference Material 2390, DNA Profiling Standard," American Academy of Forensic Sciences (AAFS) Workshop, San Antonio, TX, February 16, 1994.

Richie, K.L., "Measurement Technology and Standards for 'DNA Fingerprinting'," National Organization of Black Chemists and Chemical Engineers, Atlantic City, NJ, April 5, 1994.

Ridge, K.D., "Formation of a Light-Stable and Functional Rhodopsin," Otsuka America Pharmaceutical, Inc., Rockville, MD, April 11, 1994. Invited

Ridge, K.D., "Achieving a Folded and Functional Rhodopsin," Center of Marine Biotechnology, UMBI, Baltimore, MD, April 13, 1994. Invited

Ridge, K.D., "*In vivo* Assembly of Rhodopsin-Like Complexes from Independently Expressed Protein Fragments," Max-Planck-Institute for Biophysics, Frankfurt, Germany, June 21, 1994. Invited

Ridge, K.D., "*In Vivo* Assembly of Rhodopsin-Like Complexes from Independently Expressed Protein Fragments," VIth International Conference on Retinal Proteins. Leiden, The Netherlands, June 23, 1994. Invited

Robertson, B., "Mechanism for Cell-Field Interactions," Symposium on Topics in EMF Research, Dept. of Energy, Washington, DC, May 23, 1994.

Robertson, B., "Bacteriorhodopsin Retains its Light-Induced Proton-Pumping Function after Being Heated to 140°C.," Chemical Physics Group, Tata Institute for Fundamental Research, Bombay, India, September 22, 1994.

Robertson, B., "Rapid pH Change Due to Bacteriorhodopsin Measured with a Tin-Oxide Electrode," International Conference on Molecular Electronics and BioComputing, Goa, India, September 26, 1994.

Schwarz, F.P., "Biothermodynamics at CARB," at Life Technologies, Inc., Gaithersburg, MD, September 22, 1994. Invited

Schwarz, F.P., "Thermodynamics of Lysozyme Antigen Binding to Antibodies and Their Fab and Mutated Fv Antibody Fragments," 49th Annual Calorimetry Conference, Santa Fe, NM, August 1, 1994.

Schwarz, F.P., "Thermodynamics of Cyclic Nucleotide Binding to the Mutants of Cyclic AMP Receptor Protein," Satellite Symposium on Protein, Structure, Function Engineering of the 16th International Congress of Biochemistry and Molecular Biology," Bose Institute, Calcutta, India, September 17, 1994. Invited

Tellez, C., Cabezas, H., and Guzman, R., "Modeling Affinity Partitioning of Metal Ions in Aqueous Polymer/Salt Two-Phase Systems," 207th American Chemical Society National Meeting, San Diego, CA, March 15, 1994.

Vilker, V., "Biocatalysis with Cytochrome P450 Monooxygenase," International Meeting on Chemical Engineering and Biotechnology (DECHEMA), Frankfurt am Main, Germany, June 6, 1994.

Vilker, V., "Biocatalysis with Cytochrome P450 Monooxygenase," University of Leipzig, Leipzig, Germany, June 9, 1994.

Vilker, V., Grayson, D., Koe, G. and Wong, L., "Biocatalysis of Non-Native Substrates by P-450_{cam}," 10th International Symposium on Microsomes & Drug Oxidations, Toronto, Canada, July 21, 1994.

Weetall, H., "Biosensors," University of Maryland, College Park, MD, October 26, 1993.

Weetall, H., "Bioelectronics," ACS National Meeting, San Diego, CA, March 15, 1994.

Weetall, H., "Sensors, Bacteriorhodopsin and Sensing Technology," NATO Conf. on Anal. Sensors, Florence, Italy, April 18, 1994.

Weetall, H., "Biosensor Technology," Georgetown University, Washington, DC, April 15, 1994.

Weetall, H., "Biosensor Technology," FDA, Washington, DC, May 3, 1994.

Weetall, H., "Biosensor Program at NIST," Northeastern University, Boston, MA, May 5, 1994.

Weetall, H., "View of Biosensor Technology for the Year 2010," NASA Meeting on Sensors 2000, Santa Clara, CA, May 19, 1994.

Weetall, H., "Molecular Electronics for Sensors," Gordon Research Conference on Bio/Analytical Sensors, New London, NH, July 17, 1994.

Wladkowski, B.D., "Energetics and Dynamics of Gas-Phase S_N2 Reactions," Chemistry Department, Iowa State University, Ames, IA, November 15, 1993. Invited

Wladkowski, B.D., "Phosphate Ester Hydrolysis: Understanding Enzyme Catalysts Using Computational Techniques," Chemistry Department, Western Maryland College, Westminster, MD, December 9, 1993. Invited

Wladkowski, B.D., "Phosphate Ester Hydrolysis Catalyzed by Ribonuclease A, I. Transphosphorylation: Computational Study using *Ab Initio* Effective Fragment Potentials," NCI-FCRFDC Division, Frederick, MD, September 27, 1994. Invited

Wong, L. and Vilker, V., "Behavior of Redox Proteins at the Solid Electrode Interface," Annual American Institute of Chemical Engineers Meeting, St. Louis, Missouri, November 9, 1993.

3. Cooperative Research and Development Agreements (CRADA) and Consortia

Applications of Image Plate Technology to X-ray Data Collection, G.L. Gilliland
Quantex Corporation (CRADA)

Biopharmaceutical Engineering Research Center, H.H. Weetall
University of Kentucky (CRADA)

Consortium on Advanced Biosensors, H.H. Weetall
Abbott Laboratories (CRADA)
Becton Dickinson Advanced Diagnostics (CRADA)
Ciba Corning Diagnostics Corporation (CRADA)
Dow Chemical Company (CRADA)
DuPont Medical Products (CRADA)
Miles, Inc. (CRADA)
Ohmicron (CRADA)

Development of Advanced Computing Technology in Software for Protein Crystallography and Computational Chemistry, W.J. Stevens
IBM Corporation and Mt. Sinai Medical School (CRADA)

Development of Generic Technologies for Construction of Enzyme-Based Electricochemical Biosensors, S. Glazier
The Nitrate Elimination Co. (CRADA)

Development of Purification Methods for Therapeutic Plasma Proteins, H. Cabezas, Jr. and K.D. Cole
Jerome H. Holland Laboratory of the American Red Cross (CRADA)

Differential Scanning Calorimetry Determination of Glass Stability, F.P. Schwarz
Life Technologies, Inc. (CRADA)

Model Bilayer Membranes in Surface Plasmon Resonance Studies of Cell Membrane Receptor Proteins, A.L. Plant
Smith-Kline Beecham Pharmaceuticals (CRADA)

NMR Structure Analysis of Bacterial Polysaccharides, B. Coxon
Univax Laboratories, Inc. (CRADA)

Research on Bacteriorhodopsin, H.H. Weetall
University of Wisconsin (CRADA)

The Integration of Software and Graphics for Structural Biology, G.L. Gilliland
IBM Corporation (CRADA)

4. Patent Awards and Applications

Allen, R. and Reeder, D.J., "Matrix Modification in the Electrophoretic Separation of Nucleic Acids" (allowed April 1994).

Hancock, D.K. and Reeder, D.J., "Ion Specific Chelating Agents Derived from β-Hydroxyhistidine, 4-(1-Hydroxy-1-Alkyl)Imidazole and Derivatives Thereof" (allowed June 1994).

Penn, L., Weetall, H., McCurley, M., Plant, A., and Glazier, S., "Chromatography Column Sensors" (submitted by Univ. of Kentucky, Case No. 657).

Plant, A., Locascio-Brown, L., and Durst, R.A., "Liposome Inmmunoanalysis by Flow Injection Assay" (allowed July 1994).

5. SRM Activities

SRM 2390 DNA Profiling Standard

6. SRD Activities

SRD 21 NIST/NASA/CARB Biological Macromolecules Crystallization Database (Update)

7. Calibrations

None

8. Committee Assignments

H. Cabezas

Scientific International Committee for the Conference on Advances in the Uses of Polymers in Cell Biology, Biotechnology and Environmental Sciences

B. Coxon

ASTM Sub-committee E 13.07 on NMR Spectroscopy (Secretary)
Washington NMR Group (Committee Member)

G.L. Gilliland

NASA Microgravity Science STS-62 Protein Selection Committee 1993-1994
Reviewer of SBIR's as member (since 1991) of the Multidisciplinary Special Emphasis Panel (Special Study Section 6C) of the National Institutes of Health
Reviewer of DoE OHER Research Projects in the Structural Biology Program
1994 Candidate Selection Committee for Biological Macromolecule Special Interest Group of the American Crystallographic Association (Member)

R. Goldberg

Local Arrangements Chair of the Calorimetry Conference
IUPAC Commission on Thermodynamics (Titular Member)
IUPAC Steering Committee on Biophysical Chemistry (Member)
ASTM E48 on Biotechnology (Member)

D.K. Hancock

International Commission for Uniform Methods of Sugar Analysis (ICUMSA), Subject 4 - Polarimetry and Quartz Plates (Associate Referee)
U.S. Referee, National Committee on Sugar Analysis, Subject 4 - Polarimetry and Quartz Plates

B.C. Levin

- ASTM E-48 on Biotechnology
- NIST Chapter of Sigma Xi (President June 1993 - June 1994)
- NIST Chapter of Sigma Xi (Executive Board Member)
- NRC/NAS Committee on Improved Fire and Smoke Resistant Materials for Commercial Aircraft Interiors (Member)
- US Technical Advisory Group to ISO TC92/SC3 (Chairman through January 1994)

M. McCurley

- NSTC Biotechnology Research Submittee (Executive Secretary)
- Society of the NIST Chapter of Sigma Xi Education Committee (Member)
- ASEE/NRL Post-Doctoral Review Panel (Reviewer)

K.H. McKenney

- PhD Examining Committee, Department of Genetics, The George Washington University, Washington, DC
- Member of Executive Council of Microbial Genome Consortium
- Member of NINDS, NIH Laboratory Promotion Committee

C.D. O'Connell

- ASTM E-48 on Biotechnology

L.J. Powell

- NSTC Biotechnology Research Subcommittee (Chair)
- Advisory Committee, NIH Women's Health Initiative (ex officio member)
- ASTM E-48 (1st Vice Chair)
- ACS Biochemical Technology Division (Councilor)
- ACS Materials Secretariat (Delegate)

P. Reddy

- PhD Examining Committee, Department of Genetics, The George Washington University, Washington, DC

D.J. Reeder

- ASTM E-48 on Biotechnology
- Advisory Committee for the Institute of Forensic Anthropology and Human Identification
- CAP Forensic Identity Subcommittee
- NCCLS Ancillary Committee on Molecular Biology
- Technical Working Group on DNA Analysis Methods (TWGDAM) Quality Assurance Subcommittee

F.P. Schwarz

NSF Review Committee for Proposals submitted to Division of Molecular & Cellular Biosciences

National Institutes of Health/Alcohol, Drug Abuse, and Mental Health Administration Scientific Review Committee

Titular Member, IUPAC (International Union for Pure and Applied Chemistry) Steering Committee on Biophysical Chemical Measurements

IUPAC Sub-committee on Recommendations for the Measurement and for the Presentation of Results Obtained on Biological Substances with Scanning Calorimetry (Chair)

U.S. Calorimetry Conference Organizing Committee

Board of Examiners for Ph.D. Thesis, Indian Institute of Technology, Hauz Khas, Delhi, India

Research Conferment for Evaluation of Ph.D. Thesis, Molecular Biophysics Unit, Indian Institute of Science, Bangalore, India

W.J. Stevens

DoE Peer Review Panel for High Performance Computing (Member)

Y. Tewari

ASTM Committee E-48 on Biotechnology (Member)

Calorimetry Conference Organizing Committee (Member)

9. Editorships

H. Cabezas, K.D. Cole, and J.B. Hubbard

Special volume of the Journal of Chromatography, developed from the "Workshop on Chromatography, Electrokinetics, and Separations in Porous Media"

M.M. Dizdaroglu

Free Radical Research

D.J. Reeder

Applied and Theoretical Electrophoresis

H.H. Weetall

Applied Biochemistry and Biotechnology (Executive Editor)

10. Seminars

October 7, 1993

Dr. Claude DesLouis, Physique des Liquides et Electrochimie, Université P. et M. Curie, Paris, France, "Charge Transport Through Polyanaline Films." (Division Sponsor: A. Gaigalas)

November 15, 1993

Dr. Mark Batzer, Lawrence Livermore National Laboratory, Livermore, CA, "Alu Repeats as Tools for Molecular Archeology." (Division Sponsor: D. Reeder)

November 17, 1993

Prof. Barry Halliwell, University of London King's College, "Free Radicals in Human Disease: Measurement and Significance." (Division Sponsor: M. Dizdaroglu)

November 17, 1993

Dr. Robert Lipshutz, Affimetrix, Inc., Santa Clara, CA, "Oligonucleotide Arrays and Sequence Analysis by Hybridization." (Division Sponsor: C. O'Connell)

January 12, 1994

Prof. Larry Grossman, Johns Hopkins University, Baltimore, MD, "Dynamics of Nucleotide Excision Repair of Damaged DNA." (Division Sponsor: M. Dizdaroglu)

January 13, 1994

Dr. Noel R. Rose, Johns Hopkins University, Baltimore, MD, "Virus-Induced Autoimmune Disease." (Division Sponsor: H.H. Weetall)

January 13, 1994

Dr. Tautgirdas Ruzgas, Institute of Biochemistry, Vilnius, Lithuania, "Adsorption of Heme-Peptides and Proteins at Solid/Liquid Interfaces." (Division Sponsor: A. Gaigalas)

January 26, 1994

Dr. Sergei D. Varfolomeyev, Department of Chemistry, Moscow State University, Moscow, Russia, "Bioelectrocatalysis, Direct, Electronic Contacts between Enzyme, Active Site and Conduction, Biosensors and Cellsors." (Division Sponsor: H.H. Weetall)

March 10, 1994

Professor Hans-Jurgen Hinz, Institut fur Physikalische Chemie, Munster, Germany, "Folding Studies on Native and Mutated Proteins." (Division Sponsor: F.P. Schwarz)

March 11, 1994

Dr. Linda Malkas, University of Maryland/Baltimore, "Mammalian Cell DNA Replication." (Division Sponsor: G.L. Gilliland)

March 14, 1994

Dr. Clare Woodward, University of Minnesota, "The Hydrogen Exchange Core is the Protein Folding Core." (Division Sponsor: G.L. Gilliland)

March 21, 1994

Dr. Kenneth Merz, Pennsylvania State University, "Computer Simulation of Biomolecular Systems." (Division Sponsor: G.L. Gilliland)

March 25, 1994

Dr. Jeffrey D. Evanseck, Harvard University, Boston, MA, "The Influence of Structural Fluctuations on Enzymatic Catalysis: A Quantum and Molecular Dynamics Study." (Division Sponsor: W.J. Stevens)

March 28, 1994

Dr. Janet Smith, Purdue University, "Structure of the Allosteric Enzyme Controlling Purine Biosynthesis." (Division Sponsor: G.L. Gilliland)

March 30, 1994

Dr. Steven Akman, City of Hope National Medical Center, Durate, CA, "Studies of Promutagenic Oxidant-Induced DNA Damage." (Division Sponsor: M. Dizdaroglu)

April 1, 1994

Dr. Celia A. Schiffer, Laboratory of Physical Chemistry, ETH Zentrum, Zurich, Switzerland, "Determining Flexibility and Stability of Protein Structure Using Molecular Dynamics." (Division Sponsor: W.J. Stevens)

April 4, 1994

Dr. Timothy F. Havel, Harvard Medical School, Boston, MA, "Recent Developments in Distance Geometry and NMR Analysis." (Division Sponsor: W.J. Stevens)

April 6, 1994

Dr. Michael Gilson, University of Houston, Houston, TX, "Computer Simulations of Biomolecules." (Division Sponsor: W.J. Stevens)

April 7, 1994

Kerstin Skowasch, Roche Molecular Systems, Alameda, CA, "Mitochondiral DNA." (Division Sponsor: D.J. Reeder)

April 8, 1994

Dr. S. Subbiah, Beckman Laboratories, Stanford University School of Medicine, Stanford, CA, "Sequence-Structure Constraints in the Evolution of Protein Architecture." (Division Sponsor: W.J. Stevens)

April 18, 1994

Dr. Ann Ginsberg, National Institutes of Health, Bethesda, MD, "Thermally Induced Unfolding of the Tryptophan Synthase Multienzyme α_2B_2 Complex from S.typhimurium." (Division Sponsor: F.P. Schwarz)

April 25, 1994

Prof. Marcia Newcomer, Vanderbilt Univ. School of Medicine, "Protein-Retinold Interactions: The Structural Basis for Retinoid Binding Recognition." (Division Sponsor: G.L. Gilliland)

April 26, 1994

Dr. Laura Moen, Old Dominion University, Norfolk, VA, "HIV-1 Reverse Transcriptase: Studies on a Recombinant Deletion Mutant." (Division Sponsor: W.J. Stevens)

May 2, 1994

Dr. Robert Phillips, University of Georgia, "Structure and Mechanism of Tyrosine Phenol Lyase." (Division Sponsor: G.L. Gilliland)

May 4, 1994

Dr. Patrick Loll, "X-ray Structure of the Integral Membrane Protein Prostaglandin H_2 Synthase." (Division Sponsor: G.L. Gilliland)

May 9, 1994

Dr. Masao Fujinaga, University of Alberta, "Structure of Seryl-tRNA Synthase from Thermus thermophilus." (Division Sponsor: G.L. Gilliland)

May 16, 1994

Dr. Nadik Abdulaev, Shemyakin Institute of Bioorganic Chemistry, Moscow, Russia, Conformational Changes of Rhodopsin as Probed with Monoclonal Antibodies." (Division Sponsor: K.D. Ridge)

May 16, 1994

Ravi Viswanathan, Department of Chemical Engineering, University of California at Santa Barbara, Santa Barbara, CA, "Structural Characterization of Organic Thin Films by the Atomic Force Microscope." (Division Sponsor: A. Plant)

May 19, 1994

Dr. Thomas Poulos, University of California at Irvine, Irvine, CA, "Peroxidase and P-450: Structure, Function and Engineering." (Division Sponsor: W.J. Stevens)

July 27, 1994

Amit Chattapadhyay, Centre for Cellular & Molecular Biology, Hyderabad, India, "Anatomy of an Ion Channel." (Division Sponsor: J. Kasianowicz)

August 4, 1994

Dr. Elena Ya. Korchemskaya, Institute of Physics, Ukrainian Academy of Sciences, Kiev, Ukraine, "Photoinduced Anisotropy in Bacteriorhodopsin Films. Polarization and Holographic Properties of Bacteriorhodopsin Films in Optical and Biomedical Applications." (Division Sponsor: H.H. Weetall)

August 13, 1994

Dr. Celia Bonaventura, Marine Biological Center, Duke University, Beaufort, NC, "Marine Biotechnology." (Division Sponsor: H.H. Weetall)

September 21, 1994

Prof. Steven M. Cramer, Isermann Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, NY, "Novel Low Molecular Weight Displacers For Protein Purification in Ion Exchange Systems." (Division Sponsor: H. Cabezas)

September 26, 1994

Dr. Jack Collins, National Cancer Institute, Frederick, MD, "Simulations of Large-scale Motions in Proteins: Flap Dynamics in HIV-1 Protease." (Division Sponsor: K.D. Ridge)

September 30, 1994

Dr. Liang-Hong Guo, Department of Chemistry, University of Rochester, Rochester, NY, "Organized Strucutures and Solid Surfaces; Preparation, Characterization and Application." (Division Sponsor: A. Plant)

11. Conferences/Workshops/Sessions Sponsored/Co-Sponsored

October 1993

Genome Projects Session of the Human Genome Sequencing Conference, Hilton Head, SC (K.H. McKenney)

October 13-26, 1993

Macromolecular Crystallography, a Cold Spring Harbor Laboratory Workshop, Cold Spring Harbor, NY (G.L. Gilliland)

June 23-26, 1994

Co-chairman of "Workshop on Computation Chemistry of Large Molecules, Wroclaw, Poland (M. Krauss)

August 4, 1994

Academic/industrial/government Working Group on Validation of Chromatographic Separation Processes, NIST, Gaithersburg, MD (H. Cabezas, Jr.)

August 4-5, 1994

Workshop on Chromatography, Electrokinetics, and Separations in Porous Media, NIST - Gaithersburg (H. Cabezas, Jr., K. Cole, and J. Hubbard)

September 17-21, 1994

Microbial Genome Session of the Genome Sequencing and Analysis Conference VI, Hilton Head, SC (K.H. McKenney)

12. <u>Other</u>

V. Vilker
Professor, University of California, Los Angeles, CA

II. Chemical Kinetics and Thermodynamics Division (833)

Sharon G. Lias, Chief

A. Division Overview

The Chemical Kinetics and Thermodynamics Division is the primary resource within the Chemical Science and Technology Laboratory for expertise and information on topics related to physical chemistry, especially chemical kinetics and thermodynamics. The programs of the Division are directed to experimental measurements of key kinetic and thermodynamic quantities, and the development of measurement techniques and methodologies. The most important mechanism for disseminating Division output to the scientific and technological public is through the generation of databases of high quality evaluated numeric data. Both experimental research and database-building activities are focussed on problems of national importance, such as effects of pollutants on the earth's atmosphere, industrial chemical processing, biological and medical processes, and synthesis of materials.

The work of the Division is carried out by 52 chemists and 5 supporting personnel (28 NIST employees, 22 full-time Guest Researchers, one on-site contractor, and two on-site Cooperative Research Grantees), who have expertise in gas and liquid phase kinetics, thermodynamics, optical and mass spectroscopy, and computational chemistry. The Division is made up of 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. The Division also has a strong expertise in the generation of expert software for use with chemical databases. The link between the experimental programs and the work of the Data Centers is strong, since most senior Division scientists are actively involved in both experimental and data evaluation projects. The expertise and insight needed for reliable data evaluation are most often found in scientists who are experienced in experimental work, and therefore, the considerable breadth of ongoing experimental activities in the Division provides a fertile resource for the data evaluation activities. The expertise in computational chemistry available in the Division supports both experimental and data evaluation work.

The Chemical Kinetics and Thermodynamics Division serves as a technical resource on environmental, industrial processing, energy, analytical chemistry, and chemical database problems for a wide range of external organizations and companies. In FY94, 39% of Division research was supported by other agencies and industry, notably including the Department of Energy (DoE), the National Aeronautics and Space Administration (NASA), the Environmental Protection Agency (EPA), the Department of Defense (DoD), SEMATECH (the industry-government consortium for advancing **SE**miconductor **MA**nufacturing **TECH**nology), and the Sadtler Division of the Bio-Rad Corporation. Another 22% of Division work was supported by the NIST Standard Reference Data Program (SRDP).

The on-going work in the Division, including both experimental and data evaluation activities, ties to one or more of the strategic thrusts of the Chemical Science and Technology Laboratory. In particular, Division work is relevant to: **environmental technology and concerns, fundamental measurement technology, industrial processes**, and **health care technology**. Some projects, such as those dealing with **analytical chemistry, computational chemistry** and **chemical database development**, may have applications in several - or all - of these thrust areas.

The single most important thrust of the programs of the Chemical Kinetics and Thermodynamics Division is **environmental research**. Data and experimental research on gas phase kinetics is important to an understanding of atmospheric chemistry. Work on the effects of man-made chemicals on the earth's ozone layer began in our laboratories in the early 1970's, and has continued to the present. 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. Dr. Michael Kurylo is also serving as Program Manager/Program Scientist for the 1994 Airborne Southern Hemisphere Ozone Experiment (ASHOE), being conducted in concert with the Measurements for Assessing the Effects of Stratospheric Aircraft (MAESA) program.

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. A new project initiated this year in the Chemical Thermodynamics Group is directed to the determination of the thermodynamic properties of aqueous solutions at temperatures lower than the freezing point of water. There is a paucity of data on such solutions, although a knowledge of the thermodynamics is necessary to understand the role of heterogeneous reactions occurring on the surface of ice crystals in the atmosphere. Both the Chemical Thermodynamics Data Center and the Chemical Kinetics Data Center include comprehensive data evaluation efforts aimed at providing high quality data for use in modeling/predicting processes in the upper atmosphere, especially those relevant to modeling stratospheric ozone layer perturbations. Much of this work is carried out in concert with NASA's Upper Atmosphere Research Program.

A long-term project sponsored by the Department of Energy involves 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 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. This unique research provides the detailed understanding of photosynthesis processes - and detailed recipes for how to reproduce these processes - which will be essential if solar energy conversion is ever to be commercially exploited as a practical energy source.

Another DoE-sponsored project with important environmental implications is the evaluation of data on the kinetics of combustion processes. The goal of this project is the production of a complete, self consistent evaluated database of kinetic data for use in the modeling of hydrocarbon combustion.

During FY94, under a Cooperative Research Agreement with Stanford University, a new facility was constructed in Division laboratories to exploit degenerate four wave mixing (DFWM) spectroscopy as a means of measuring spacial and temporal concentrations of chemical species in hostile environments - such as plasmas and flames - that thwart other spectroscopic measurements. Four-wave mixing spectroscopy can measure molecular concentrations remotely and can cope with the cumbersome optical geometries that commercial reactors, incinerators, and other gas-phase processing equipment impose. In the coming year, the emphasis of the research will be on understanding processes occurring in non-thermal plasmas. Such plasmas represent a promising new technology for the control and destruction of volatile organic compounds and other atmospheric pollutants. The DFWM spectroscopy work, relevant to both **environmental** and **process technology** thrusts, is related to another on-going project, the development of a database for dry etching and semiconductor manufacture.

Other work relevant to **industrial processes** includes a new project initiated with CSTL Director's Reserve funding. The project is dedicated to providing calorimetric determinations of the thermodynamic properties of specific compounds identified by the Design Institute for Physical Property Data (DIPPR); DIPPR is a 42-company industrial consortium set up for the purpose of developing a high quality set of critically evaluated thermodynamic data for pure compounds and mixtures. DIPPR projects are initiated by member companies in response to industrial needs in areas which suffer most acutely from the lack of reliable thermodynamic data. Member companies have compiled a list of some 1500 compounds for which thermodynamic measurements are badly needed. Because of the compatibility between the goals of DIPPR and those of the Chemical Thermodynamics Group, we initiated experimental work on a set of these compounds after conferring with the leadership of DIPPR. The new project, which was initiated in May, is related to pre-existing DIPPR projects on "Pure Component Ideal Gas Enthalpies of Formation", "Data Compilation", and "Data Prediction Methods". An expansion of the DIPPR collaboration to include data evaluation activities is anticipated.

Another thermodynamics project initiated this year with support from the Director's Reserve is directed to building a new database of thermochemical data on chalcogenides. Chalcogenides are inorganic compounds in common use in industry, for example as hydrogenation catalysts, adsorbents for waste water and waste gas, components of photoelectric cells, intercalation compounds, raw materials in steel manufacture, and light sensing materials in laser- and optical-recording devices and batteries. The only available source of data on these compounds is 20 years out-of-date.

Division work relevant to **health care technology** centers primarily on studies of the kinetics and mechanisms of the reactions of free radicals in condensed phase systems. The importance of such reactions in biological processes has become apparent within the past few years. The only way such reactions can be studied directly is with the use of pulsed high energy electron sources (pulse radiolysis) to generate radicals and observe their reactions. The Division pulsed radiolysis facility is one of the few laboratories equipped to carry out experimental examinations of such reactions.

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 data project for the **analytical chemistry** community. This database of 75,000 electron mass spectra is in use in thousands of analytical chemistry laboratories throughout the world. The collection of spectra is distributed to instrument manufacturers who distribute the database in the data systems of commercial analytical mass spectrometers; we also produce a personal computer version with search software. Although the involvement of this Division - which primarily has expertise in physical chemistry - with the improvement of an analytical mass spectrometry database may seem anomalous at first glance, the physical chemistry expertise in ionic dissociation mechanisms (the primary focus of the Ion Kinetics and Energetics Data Center) is what is needed for the evaluation of electron impact mass spectra.

Work on the mass spectral 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 programs, and has led to numerous spin-off activities including new databases and software products, as well as numerous direct government-industry technology transfer activities. Because of its importance as a resource for analytical chemists, the database has, for several years, had its own Steering Committee. A meeting of this Steering Committee was held at the Pittsburgh Conference in Chicago in March. The Steering Committee includes representatives from all the major instrument manufacturing companies which distribute the NIST/EPA/NIH Mass Spectral Database, and representatives of the EPA and NIH, as well as several leading analytical chemists. Members of the Committee considered numerous technical details having to do with production of the database including the evaluation of spectra, the presentation of spectra, and software development issues.

As mentioned above, the most important mechanism for disseminating Division output to the scientific and technological public is through the generation of databases of high quality evaluated numeric data. During FY94, six computerized database products originating from the Division were released by the Standard Reference Data Program. The Division has a significant activity devoted to the **development of software for use with personal computer-based chemical databases**. This year, a significant achievement was the production of a "Dynamic Link Library" (DLL) version of the NIST/EPA/NIH Mass Spectral Database. The DLL version presents the database distributors with a prepackaged system which can be directly incorporated into a mass spectrometer without any reformatting or indexing of the data files. Software for searching the database is also provided for use in the commercial mass spectrometers for the first time. Previously, instrument manufacturers received only the database itself and provided their own software for searching the data.

Another project carried out primarily for the purpose of development of an analytical chemistry technique is the high pressure mass spectrometry effort, which provides measurements of the rates, mechanisms, and energetics of bimolecular reactions of ions in the gas phase. Such reactions are the basis for the analytical technique called Chemical Ionization Mass Spectrometry. Research on the kinetics of ion/molecule reactions carried out in these laboratories in the 1960's provided much of the early impetus for the development of the technique, and current mass spectrometric studies of the mechanisms and thermochemistry of chemical ionization processes are fully funded by the Department of Energy because of their analytical importance. The Department of Energy is interested in the development of improved methods for the analysis of fossil fuels.

During FY94, a new project devoted to the use of **computational chemistry** to generate and evaluate chemical kinetics and thermodynamics data was initiated in the Division. Initially, attention was given to a systematic examination of the accuracy and precision of different *ab initio* methods for the calculation of molecular vibrational frequencies. The continuation of this work will be directed to developing a method for the *ab initio* calculation of thermodynamic properties of organic molecules that is more accurate and reliable than Gaussian-2 theory, which is the current *de facto* standard.

Division scientists continue to hold leadership positions in the fields of chemical kinetics and thermodynamics, notably in the International Union of Pure and Applied Chemistry (IUPAC) Commissions on Thermodynamics and on Kinetics, the NASA Panel for Data Evaluation, and the Scientific Steering Committee of the International Network for the Detection of Stratospheric Change. Division members are also active on committees of the American Society for Testing Materials (ASTM) and the International Council of Scientific Unions Committee on Data for Science and Technology (CODATA). Dr. P.A.G. O'Hare is the Editor-in-Chief of the Journal of Chemical Thermodynamics, and Dr. Sharon Lias is on the Board of the American Society for Mass Spectrometry. Dr. O'Hare was the co-editor of a book entitled "Solution Calorimetry", which was published in 1994; the book is the fourth volume in the International Union of Pure and Applied Chemistry (IUPAC) series on "Experimental Thermodynamics", and includes 13 chapters by experts in the field from laboratories around the world. Dr. Eugene S. Domalski served as the Program Chairman for the 49th Calorimetry Conference which met in Santa Fe, New Mexico, July 31 - August 4, 1994. Dr. Pedatsur Neta was awarded the Department of Commerce Silver Medal for his pioneering research on solar energy storage mechanisms.

B. Selected Technical Reports (Chemical Kinetics and Thermodynamics Division)

1. 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, India), and Vladimir Orkin (Russian Academy of Science, Russia)

The Atmospheric Kinetics Laboratory carries out studies of the gas phase kinetics and photochemistry of important atmospheric constituents, especially those processes relevant to the fate of natural and anthropogenic trace gases in the troposphere and their chemical role in altering stratospheric composition. The long-term goal of this work is to generate data relevant to predicting the impact of human activities on stratospheric ozone and on global climate.

Much of the emphasis last year was directed to an examination of the atmospheric fates and environmental impact of compounds under consideration by the military for replacing fire suppressant compounds which must be phased out because of their ozone depletion potential. Most of the chemical compounds under consideration as replacements for fire suppressants and chlorofluorocarbons (CFCs) contain one or more C-H bonds. Because many such compounds are expected to degrade in the atmosphere, through reaction with OH radicals or photodissociation, to yield carbon-centered radicals that react with oxygen to produce halogenated peroxyl radicals, the atmospheric reactions of haloperoxyl radicals were determined. The conclusion derived from the results was that such radicals will most likely react with ambient NO and NO_2. Studies of peroxyl radicals in aqueous media are related, and are described in the section on the kinetics of radicals in aqueous media.

A new direction this year was the initiation of work on the atmospheric chemistry of iodine compounds. Initial studies involved the determination of the rate constant for reaction of OH radicals with CF_3I, and an exploration of the atmospheric chemistry of IO. CF_3I has been identified as a possible replacement for CF_3Br. Unlike CF_3Br, CF_3I is removed from the troposphere by photolysis or by reaction with OH, and the resulting I atoms react to form IO.

The photolytic lifetime of a molecule in the upper troposphere and lower stratosphere depends on the absorption cross section in the far ultraviolet and ultraviolet. Therefore, data on the absorption coefficients of the alternate halocarbons, both below and above the oxygen absorption cut-off, are important in predicting atmospheric lifetimes. 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 for CF_3I and CF_2ClCH_3 (HCFC-142b), CF_3CCl_2H (HCFC-123), CF_3CFClH (HCFC-124), and CH_3CCl_3 were determined.

The long-term collaborative work with researchers at the Ford Motor Companyon on the environmental effects of fuel additives continued, and a new collaboration with scientists at

Brookhaven was initiated; the latter effort is aimed at determinations of bond strengths in halocarbon compounds.

2. Kinetics Data Evaluation and Database Production: New Database Releases and Evaluation Efforts on Kinetics of the Upper Atmosphere

W.G. Mallard, W. Tsang, R.F. Hampson, J.A. Manion, K.K. Irikura, R.D. Levin, D. Frizzell, P. Christian, and J. Reed

The primary activities of the Chemical Kinetics Data Center include (1) the evaluation of kinetic data for the NASA Panel for Data Evaluation, which is the body officially designated to provide the definitive evaluated data for use in modeling the chemistry of the upper atmosphere, and for the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry; (2) the development of a complete database of self-consistent, evaluated kinetic data for use in the modeling of hydrocarbon combustion; and (3) the production of computerized chemical kinetics database products.

The single most important dissemination mechanism for Data Center collections and evaluations is the NIST Chemical Kinetics Database, which is distributed by the Standard Reference Data Program as a personal computer database with software developed in the Data Center. Work was completed on Version 6.0 of the Chemical Kinetics Database, containing data relating to over 8800 reactant pairs, and the update is to be released early in FY1995. Work on production of a Windows version of the product is progressing. The database has sold more than 1000 copies since its initial release, making it the best-selling personal computer database distributed by the Standard Reference Data Program.

Version 2.0 of the solution kinetics database, developed in collaboration with Notre Dame Radiation Laboratory (NDRL) and Division members R. E. Huie and P. Neta, was released during the year. The update includes data reported in the literature through the end of 1992. The database contains more than 14,300 rate determinations for over 10,800 reactions. The update also includes improved software with new search modes. A compilation of rate constants for reactions of carbon-centered radicals is being prepared for publication in the Journal of Physical and Chemical Reference Data, and for addition into the solution kinetics database.

Calculational projects carried out in collaboration with Dr. M. Zachariah of the Process Measurements Division included studies of nucleation kinetics and examinations of the kinetics in high temperature $Si_xH_yO_z$ reactions. A new, more accurate additivity scheme for the prediction of the gas phase enthalpies of formation of chlorinated alkanes, alkenes, and alkynes, was developed, and a manuscript describing the results was prepared. Work proceeded on the preparation of an expanded and updated evaluation of chemical kinetics and photochemical data for the NASA Panel for Data Evaluation.

3. Kinetics and Dynamics of Plasmas: Optical Detection of Reactive Intermediates Using New Degenerate Four-Wave Mixing Facility

J.W. Hudgens, R.D. Johnson III, J.L. Brum, and D.S. Green (Stanford University)

In 1994, a new degenerate four-wave mixing (DFWM) facility was constructed to be used as a remote sensing diagnostic technique. Four wave mixing spectroscopies are capable of detecting and monitoring chemical species in hostile environments, such as flames, plasmas, and flue gases from boilers. The technique has many advantages, such as high spatial, spectral, and temporal resolution. In addition, no intereferences can arise from species outside the sample region. DFWM is also a form of real-time holography that is suitable for 3-dimensional imaging. Initial proof-of-principle experiments were completed, using NH radical spectra to profile the evolution of gas mixtures containing ammonia, hydrogen or fluorine, and argon passed through a microwave discharge.

The project will focus on the characterization of chemical processes occurring in plasmas. Most plasmas are highly luminous and are characterized by steep gradients in temperature and concentration, conditions which thwart fluorescence and absorption diagnostics. In addition, in many plasma reactors the electrodes and associated electronics impose cumbersome optical geometries. Using the new facility, these problems can be sidestepped; sensitive and spatially resolved measurements of concentration and temperature can be made. Used in conjunction with computer simulations, this approach can lead to an understanding of fundamental chemical processes occurring in plasmas. A standardized plasma reactor (the "Gaseous Electronics Conference Radio-Frequency Reference Cell") is being acquired, and will be used for experimental work in the coming year.

Other studies this year included an examination of spectroscopic detection schemes of a number of radicals using the resonance enhanced multiphoton ionization (REMPI) technique. Species studied included AsF, AsCl, PF, HCF and DCF, and BH and BD. Newly discovered REMPI spectra form the basis of new sensitive and selective schemes for the optical detection of these radicals.

4. A New Project on Calorimetric Measurements for Industry

D.R. Kirklin and P.A.G. O'Hare

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. The Division has two calorimetry laboratories devoted to providing this kind of information, namely, the precision oxygen bomb calorimetry laboratory and the unique fluorine bomb calorimetry facility, which is the only operating facility of its kind in the world.

A new project was initiated in 1994 to provide calorimetric determinations of the thermodynamic properties of specific compounds for an industrial consortium, the Design Institute for Physical

Property Data (DIPPR). DIPPR has compiled a list of 1500 compounds for which thermodynamic information is specifically needed by consortium member companies. Initial work involved determining the enthalpies of combustion and formation for acetylsalicylic acid, acetaminophen, ibuprofen, and trimellitic anhydride. As part of this project, a methodology was developed to use differential scanning calorimetry measurements to extend the measurements on solids to the liquid and vapor phases.

In 1994, work continued on the determination of heats of combustion of organic compounds containing both phosphorus and sulfur. These data are needed to develop a reliable estimation scheme for predicting the thermodynamic properties of organic phosphorus compounds not amenable to experimental measurements because of their hazardous properties. The U. S. Army, in particular, needs such data in order to design methods for the destruction of chemical agents. The NIST oxygen bomb calorimetry laboratory is the only laboratory that has the capability for carrying out bomb calorimetric measurements on these organic compounds. Measurements on the enthalpy of formation of triphenylphosphine sulfide (TPPS) were completed; the separation and analysis of the combustion products required the development of an ion chromatographic method. The gross calorific value, ash content, and moisture content of Standard Reference Material Coals 2683a and 2684a were certified in 1994.

5. The NIST/EPA/NIH Mass Spectrometry Data Center: Release of New Software Innovations

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), and T.F. Levitskaia (Moscow Institute of Radiotechniques, Russia)

This Data Center maintains and improves the NIST/EPA/NIH Mass Spectral Database, develops software for searching the database, carries out research to evaluate and develop spectral matching algorithms, and evaluates mass spectral data. The database, a collection of 75,000 spectra of 62,235 compounds, is distributed to instrument manufacturers who make it available to their customers as an integral part of the data systems of commercial mass spectrometers. The collection is also available as a personal computer database package with search software designed in the Data Center.

In 1994, the Data Center completed three major software innovations for use with the Mass Spectral Database. The new "Dynamic Link Library" (DLL) version was made available to the instrument manufacturers for the first time. This version presents the database distributors with a prepackaged system which can be directly incorporated into a mass spectrometer without any reformatting or indexing. Software for searching the database is also provided for use in the commercial mass spectrometers for the first time. Previously, instrument manufacturers had to reformat and index the data files received from NIST, and also had to write and maintain software for searching the files. Because of these procedures, the incorporation of a new update of the NIST database was expensive and slow. The DLL version of the database will effect a large savings in time and effort for the distributors of the database.

Another innovation was presented in the release of version 4.5 of the personal computer (PC) version of the database, which incorporates improvements in the software used to search the database. New features include a more efficient way of searching the database, a file of 12,000 replicate spectra, and a new "incremental" name search, which makes it easy for the user to type the name correctly and observe other similar compound names in the system. New improved documentation was also provided.

At the end of the year, a new version of the personal computer database for use with Microsoft Windows was submitted for release early in 1995. This major release, which had been under preparation for two years, provides new search systems, optimized spectrum matching algorithms, and many other new features which will increase the flexibility and efficiency of use of the database.

The comprehensive study of algorithms used for matching unknown spectra against mass spectral databases was completed and published in 1994. Five algorithms were systematically tested against the database using a test set of 12,592 evaluated spectra. Interestingly, the two algorithms in the set which were specifically designed for use with mass spectra were found to give the worst performance. The results of this study may impact on the choice of search algorithms used by instrument manufacturers in the data systems of commercial mass spectrometers.

In 1994, the long-term evaluation of all the spectra in the database continued; 20,000 of the unique spectra in the collection have been examined, and only 5,000 remain to be evaluated. Numerous problems and errors have been uncovered and the problem spectra have been deleted from the collection, or appropriate corrections have been made. There has been a major increase in the quality of the NIST/EPA/NIH Mass Spectral Database as a result of the systematic evaluation effort. The next update of the underlying database (as opposed to a software update) is scheduled for late summer of 1995. The size of the updated database will approach 100,000 spectra.

The NIST/EPA Vapor Phase Infrared Database is produced as a spin-off of the mass spectral database; that is, when original spectra are determined in-house for the mass spectral database, the instrument which is used is capable of producing at the same time an infrared spectrum of the compound. Since the determination of spectra is carried out only as an additional step in a process occurring for the mass spectral database, the work involved in processing the spectra (retrieval of Chemical Abstracts Registry Numbers, production of structural drawings, entry of names and synonyms into a database, etc.) does not have to be duplicated. Work on enlarging this database continued routinely during the year.

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

R.W. Carter and D.G. Archer

A facility is under construction for a new project that has as its objective the determination of thermodynamic data on aqueous solutions of acids, salts,and related mixtures in the temperature range from 25 °C to -75 °C. 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 in the atmosphere. Thermodynamic data on such solutions are abundant for the temperature range above room temperature (25 °C to 300 °C), but are almost non-existent for temperatures below room temperature.

A differential scanning calorimeter facility has been set up, and a flow calorimeter is being constructed. Initial experiments will be dedicated to measurements of the heat capacities of supercooled aqueous sodium bisulfate, sulfate, and nitrate solutions.

7. Thermodynamic Properties of "High Tech" Materials: Completion of New Heat Capacity Facility

D.G. Archer, P.A.G. O'Hare, D.R. Kirklin, and I. Zieborak-Tomaszkiewicz (Institute of Physical Chemistry, Poland), and E.J. Cotts (State University of New York at Binghamton)

During 1994, a new low temperature heat capacity calorimetry facility was completed. This new facility, along with the existing bomb calorimetry laboratories, makes the NIST thermodynamics laboratories one of only two laboratories in this hemisphere with the capacity to carry out the full range of measurements necessary to predict chemical equilibrium constants for systems of interest. Equilibrium constants of a chemical reaction give information about the extent of reaction (how much product and reactant are present at chemical equilibrium) needed in setting up large-scale industrial processes such as fossil-fuel refining, large-scale amino acid production, corrosion, and inorganic chemical production.

Data on standard molar enthalpies of formation of "high-tech" materials, which are often amorphous (glassy), in many cases can not be determined by oxygen bomb calorimetry. However, using the technique of fluorine-combustion calorimetry, the exceptional oxidizing power of fluorine permits the experimental determination of the enthalpies of formation of such substances. The NIST fluorine bomb calorimetry facility has as its aim the establishment of benchmark thermodynamic information for pure materials of importance in modern technologies. This year, calorimetric studies were completed on $W_5Si_{3.12}$, GeTe, GeS, and Mo_3Si. The results will help elucidate the behavior of these materials under conditions used in industrial processes.

The enthalpy of formation and heat of combustion of $TiSi_2$ was successfully determined using oxygen bomb calorimetry with magnesium as an ignition source, and the new low temperature heat capacity facility was used to measure the enthalpy increments for this compound over the temperature range from 5 to 350K. Other very high quality measurements from the new facility were completed for copper and aluminum oxide.

8. Chemical Thermodynamics Data Evaluation and Database Production: New Databases and Evaluations Projects Under the Chemical Thermodynamics Data Center

D.B. Neumann, P.A.G. O'Hare, D.G. Archer, R.D. Levin, D. Frizzell, P. Christian, and J. Reed

A new data evaluation project initiated this year will generate a new database on the thermochemical properties of the chalcogenides, inorganic compounds in common use in industry as hydrogenation catalysts, adsorbents for waste water and waste gas, components of photoelectric cells (in printed circuit boards, for example), intercalation compounds, raw materials in steel manufacture, inorganic glasses, and light sensing agents in laser- and optical-recording devices and batteries. In order to understand the behavior of the chalcogenides under industrial conditions (for example, the decomposition of the high-temperature lubricant MoS_2 to the non-lubricating Mo_2S_3), quantitative data on the thermodynamic properties of the compounds are needed, but there is no up-to-date source of evaluated data concerning these properties. Dr. P.A.G. O'Hare is collaborating with scientists at Rice University and the U.S. Geological Survey to generate the new database. Last year, work focussed on the evaluation of data on GeS, GeS_2, Ge_2S_2, GeSe, $GeSe_2$, SiTe, and SiSe.

In 1994, the database "Properties of Aqueous Solutions" (subtitled "Aqueous Solutions of Electrolytes: Binary and Mixed Electrolyte Systems - Activity and Osmotic Coefficients, Excess Gibbs Energy") was released for distribution to the public by the Standard Reference Data Program. This database, prepared under the sponsorship of the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers, presents a program for the calculation of activity and osmotic coefficients, the activity of water, and excess Gibbs energies for single and mixed electrolyte solutions at 25 °C and elevated temperatures to 200 °C. A database containing equation parameters and coefficients for approximately 350 single electrolytes and a large fraction of their mixtures is included.

The on-going project, "JANNAF Thermochemical Tables for Species of Importance to Ozone Depletion," carried out in collaboration with M.W. Chase of the Standard Reference Data Program, has the goal of providing the NASA Upper Atmosphere Program with a comprehensive evaluation of the thermodynamic data for stable as well as transient species involved in the network of reactions related to the destruction of ozone in the upper atmosphere. During the year, spectroscopic and thermodynamic data were gathered for radicals containing F, Cl, Br, N, O, H and I were evaluated after computer programs used in the computation of thermal functions were improved. In addition, the standard state thermal functions for the elements O_2, H_2, Cl_2, Br_2, F_2, and N_2 at low temperatures were recomputed.

Evaluations of the thermochemical properties of $HNO_3(g)$, $DNO_3(g)$, and $H_2SO_4(g)$ have been initiated; these data are relevant to the experimental project discussed elsewhere for the determination of the heat capacities of low temperature acid solutions. In a project undertaken for the U.S. Navy, thermal functions for a number of bismuth compounds were derived.

Papers on the thermodynamic properties of the NaBr-water system and an analysis of the effect of temperature scale differences on thermodynamic properties were also published or accepted for publication last year. The paper on the NaBr system also includes new measurements of the isopiestic vapor pressures of NaBr(aq).

9. Initiation of New Efforts in Calculational Chemistry

K. Irikura, R.D. Johnson, and W.G. Mallard

A new project using computational chemistry to generate and evaluate chemical kinetics and thermodynamics data was initiated in the Division. While the overall theme of the project is a systematic examination of the accuracy and precision of different *ab initio* methods used for the calculation of molecular vibrational frequencies, several projects somewhat smaller in scope were completed. For example, a comprehensive study of the structure and thermochemistry of sulfur fluorides, SF_n and the ions, SF_n^+ ($n = 1$-5) was carried out. The parent compound, SF_6, is important in the plasma processing of semiconductors and in large electrical switches. Even though there is considerable interest in the thermodynamics of sulfur hexafluoride, there were serious discrepancies in the experimental data reported in the literature for the SF_n radicals and ions; the careful calculational study led to a set of recommended values for enthalpies of formation, standard entropies and integrated heat capacities for many of the ions and radicals in question.

Work is now continuing on the development of a method for the *ab initio* calculation of thermodynamic properties of organic molecules that is more accurate and reliable than Gaussian-2 theory, which is the the current *de facto* standard. Also, techniques of computational chemistry are being used to derive so-called "group values" to be used in additivity schemes for estimation of thermochemical data in cases where there is inadequate experimental data available to derive the estimation parameters.

10. Chemical Thermodynamics Data Evaluation and Database Production - Heat Capacities and Entropies of Organic Compounds: The Chemical Thermodynamics Data Center

E.S. Domalski

In FY94, work continued on the evaluation of thermodynamic data for organic compounds and the development of schemes for the estimation of thermochemical data. Use of estimation methods is an obvious approach to generate missing data, needed in particular for engineering applications. The widely-used second-order group-additivity estimation method, which has been applied successfully to the estimation of thermodynamic properties ($\Delta_f H°$, $C_p°$, $S°$) of molecules in the gas phase, is extended in this project to the estimation of properties in the condensed phase, especially for organic compounds containing carbon, hydrogen, oxygen, nitrogen, sulfur, and halogen atoms. A paper on the heat capacities of liquid organic compounds, including both estimation parameters and evaluated experimental data, was written in collaboration with scientists at the Institute of Chemical Technology, Prague, and the Universite Blaise Pascal/CNRS, France. This work was carried out under the sponsorship of the IUPAC Subcommittee on Thermodynamic Data and the IUPAC Commission on Thermodynamics. Other papers on heat capacities and entropies of organic compounds in the condensed phase, and on the estimation of the thermodynamic properties of organic boron, phosphorus, and silicon compounds, are in preparation.

An update of the computer database product "THERM/EST: NIST Estimation of the Thermodynamic Properties for Organic Compounds at 298.15 K - Compounds Containing the Elements C, H, N, O, S, and Halogens" was released this year. THERM/EST uses "group" values especially derived for this product in order to estimate thermochemical properties of compounds in the condensed phase. Properties covered are enthalpies of formation, entropies, and heat capacities at 298.15 K, Gibbs energies of formation, and the natural logarithm of equilibrium constants for formation reactions. THERM/EST also includes an auxiliary database with data on 1,512 species.

11. High Temperature Kinetics Studies of Incineration Systems

W. Tsang, J. Manion, V.I. Babushok (Russian Academy of Sciences, Russia), and K.K. Balasubramanian (Indian Institute of Technology, India)

This long-term project, devoted to the development of a fundamental quantitative understanding of high temperature reactions of organic compounds, took on new life in 1994 with the hire of Dr. Jeffrey Manion in late 1993, and the initiation of new projects. The long-range goal of the project is to develop an understanding of large scale phenomena such as combustion in terms of elementary thermal reactions. Experimental investigations are carried out in a unique heated single pulse shock tube.

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 some decomposition will occur. In order to model the inhibition of combustion, the decomposition reactions of fluorinated compounds and reactions of fluorinated fragments must be understood. Studies to elucidate the high temperature decomposition of fluorocarbons were conducted in FY94, with a focus on understanding the processes leading to the breaking of C-F bonds. Except for the direct elimination of HF through unimolecular decomposition, direct radical attack on C-F bonds is not a facile channel for the removal of fluorine from the carbon framework; in contrast with the picture for high temperature breakdown of hydrocarbons (where decomposition is frequently initiated by a radical attack on a C-H bond), fluorocarbons dissociate through other types of mechanism, such as carbon-carbon bond fission followed by reactions of the carbon-centered radicals.

In 1994, the experimental effort was supplemented by a modeling component. Dr. V.I. Babushok is modeling ignition behavior of fire suppressant-doped fuel systems. Dr. K.K. Balasubramanian is continuing the work aimed at developing a more fundamental understanding of the mechanism of dioxin formation during incineration.

12. Chemical Database Development: New Organic Enthalpies of Formation Database

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

Two years ago, the generic chemical database software known as "Structures and Properties" was released for distribution to the public with a small database of organic thermochemical data. The software permits one to search any chemical database by structure or substructure, as well as by formula, name or synonym, or Chemical Abstracts Registry Number. In addition, additivity estimations of gas phase enthalpies of formation, heat capacities, and entropies are made by the software without the user needing any understanding of the estimation scheme. This software has generated much interest in industrial laboratories, and in the technical public in general. Last year, attention was given to generating several comprehensive databases of information on molecular properties for distribution with this software. A major goal has been the establishment of a collection of data to serve as the basis for a new Organic Enthalpies of Formation Database. At the present time, there is no comprehensive collection of data on the enthalpies of formation of organic compounds available in a personal computer format. Several existing hard copy publications are out-of-date and significantly incomplete in their coverage of the literature. Nevertheless, the need for such a compilation is easy to see when one realizes that these publications collectively accrue many hundreds of citations each year.

During FY94, a collection of data on the enthalpies of formation of 5,500 compounds was reviewed and entered into the database for inclusion in the first release, scheduled for the summer of 1995. The database covers the thermochemical literature back to 1940. In addition, the release will include a collection of 16,000 vapor pressures and boiling points, the large database of molecular structures, names, and Registry Numbers put together for the mass spectral and infrared databases, as well as heat capacities, retention indices, and other available databases. Related efforts involve the derivation of a scheme for estimating boiling points, and a new effort focussed on the acquisition of chromatographic retention data.

13. Recent Results from the Solar Energy Conversion and Storage Project

P. Neta, J. Grodkowski (Institute of Nuclear Science, Warsaw, Poland), Gregory Khaikin (Institute of Electrochemistry, Russia), Z.B. Alfassi (Ben Gurion University, Israel), and P. Hapiot (University of Paris, France)

Metalloporphyrins have broad absorption spectra in the visible light range and also display rich redox chemistry. Therefore, many of these compounds are efficient photosensitizers for solar energy conversion and storage. Experiments elucidate individual steps in reaction mechanisms pertinent to the conversion of solar energy into chemical energy. Pulse radiolysis and laser flash photolysis techniques are used to study the kinetics and mechanisms of reactions important in the catalytic oxidation of water to oxygen and the reduction of water to hydrogen in the presence of metalloporphyrin photosensitizers.

In FY94, studies of the redox and alkylation reactions of metalloporphyrins that may be important in their use as catalysts for various processes were carried out. Experiments exploring the possibility of reducing CO_2 by a reduced metalloporphyrin and inserting CO_2 into a metal-carbon bond, which would convert the gas into an organic material were initiated.

Current studies are concerned with the reduction and alkylation reactions of rhodium porphyrins. A chain reaction was found to occur in the radiolytic reduction in alkaline 2-propanol, and a new alkylrhodium porphyrin that could not be prepared by previous methods was identified. Studies by cyclic voltammetry do not indicate efficient catalysis of CO_2 reduction by Rh-porphyrins, but some effects of CO_2 are found in these systems and are being explored.

Collaborative work with P. Hapiot (University of Paris) on the oxidation of phenols by pulse radiolysis and by electrochemistry is continuing.

14. Aqueous Free Radical Kinetics: Experimental Studies

R.E. Huie, P. Neta, and Z.B. Alfassi (Ben Gurion University, Israel)

Studies of the reactions of inorganic radicals in solution are of interest because of their role in the environment (acid rain formation, for example) and in industrial chemical processes. As described above in the discussion of the Atmospheric Kinetics Laboratory, organic peroxyl radicals are produced in the atmosphere, and studies of their gas phase chemistry were carried out this year. A knowledge of the aqueous chemistry of organic peroxyl radicals is needed for understanding the biological activity of these radicals to assess the potential toxicity of these compounds. Studies this year included work on arylperoxyl, pyridylperoxyl and vinylperoxyl radicals. All were found to have absorptions in the visible range, and correlations were found between the absorption peak and the reactivity of the radical. This work is being extended to polychlorinated aromatics, whose peroxyl radicals will be formed during radiolytic decomposition of these hazardous waste materials.

Studies of solvent effects on rate constants were continued. Earlier results on the reactions of $CCl_3O_2\bullet$ with chlorpromazine and trolox have been extended to include reactions with porphyrins and reaction of a different peroxyl radical, 2-pyridylperoxyl, with several organic reductants. The correlation of log k with solvent cohesive pressure was similar. On the other hand, reaction of a different type of one-electron oxidant, the N-methylindole radical cation, with porphyrins gave a completely different behavior, indicating differences in mechanism, i.e.,outer sphere vs. inner sphere reactions. For the methylindole/porphyrin reaction, the redox potentials were measured. Good correlation, based on the Marcus theory, was found.

15. Kinetics of Reactions Relevant to Planetary Atmospheres

A. Fahr and A. Laufer (Dept. of Energy)

This project, supported by NASA, involves the exploration of the reaction kinetics of radicals thought to play a role in carbon-rich atmospheres. A new experimental thrust aimed at measurement of the temperature dependences of absorption cross sections of unsaturated hydrocarbons and inorganic gases present in planetary atmospheres, was initiated in FY94. Such results are needed to permit correct interpretation of the ultraviolet spectroscopic data obtained from earth-orbiting satellites and telescopes or interplanetary probes. The temperature dependent UV-absorption cross sections of diacetylene, methylacetylene, propylene, vinylacetylene, and 1,3-butadiene were determined in the temperature range from about 150 K to 375 K. A signficant temperature dependence was found.

Several studies of the kinetics of the reactions of the vinyl radical were completed. An examination of isotope effects in the reaction of the vinyl radical with the fully-deuterated vinyl radical demonstrated that the combination and disproportionation reactions most likely do not have totally different transition states. In experiments carried out in collaboration with scientists at the NASA Goddard Space Flight Center, the rate constant for the reaction of the vinyl radical with hydrogen was shown to be very small, about 1×10^{-20} cm^3 $molecule^{-1}$ s^{-1}; this reaction was thought to be important in the atmospheres of both Jupiter and other outer planets.

16. Kinetic Mass Spectrometry: Accurate Determinations of Entropy Changes of Proton Transfer Reactions

L.W. Sieck and M. Mautner (Christchurch, New Zealand)

Research in the Division on the reaction kinetics of gas phase ions with neutral molecules has applications to analytical chemistry. The analytical technique known as "chemical ionization mass spectrometry" is based on the chemical reactions of ions, generated in a mass spectrometer, with "unknown" substrate molecules; reactions of interest include proton transfer, hydride transfer, and electron transfer.

This project involves measurements of ion/molecule rate constants, and equilibrium constants of ion/molecule reactions as a function of temperature, using the technique of high pressure mass spectrometry. The results give quantitative data on the acidities and basicities of isolated (e.g., gas phase) molecules, relative scales of ionization energies, and data on the thermochemistry of ionic clustering reactions. The latter information has many uses, including understanding nucleation events and the prediction of biological reactions.

During FY94, the careful re-exploration of the scale of relative proton affinities of organic molecules was continued; this work ties closely to the data evaluation effort being carried out in the Ion Kinetics and Energetics Data Center. These data on proton transfer reactions are generated by the observation of equilibrium constants in the gas phase of proton transfer reactions involving a variety of molecules. The results obtained in the NIST laboratory provided information needed for the evaluation of entropy changes associated with proton transfer reactions.

Several on-going collaborations involving the applications of ion/molecule reactions were continued last year with new research projects. An in-depth study of the cationic polymerization of isobutene was carried out in collaboration with scientists at the University of Virginia. Experiments carried out at NIST on the temperature dependence of rate constants, branching ratios, and ion structures are combined with results obtained from beam experiments and condensed phase studies at the University of Virginia. Other collaborations with this group involve studies of the cationic intracluster reactions in methanol, trimethylamine and acetonitrile. The focus is on structural stabilities within protonated clusters of hydrogen-bonded systems and cyclic non-reactive intermediates during ionic chain polymerization in olefins.

17. The Ion Kinetics and Energetics Data Center: A Re-evaluation of the Proton Affinity Database

E.P. Hunter

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. Such data have applications in understanding and modeling environments where ionization occurs such as mass spectrometry, plasmas, the ionosphere, systems under high energy irradiation, etc. The Data Center maintains collections of data on ionization energies of molecules, appearance energies of fragment ions, proton- and electron-affinities, and the thermochemistry of ionic clusters.

The data evaluation project devoted to updating the 1984 Data Center Journal of Physical and Chemical Reference Data publication on proton affinities of molecules neared completion at the end of the year. 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. New publications which appeared during the year reported values for entropy changes of proton transfer reactions, but data reported from different laboratories did not agree. Calculations were carried out to resolve the discrepancies, and some benchmark measurements were carried out in the Division high pressure mass spectrometry laboratory.

C. Outputs and Interactions (Chemical Kinetics and Thermodynamics Division)

1. Publications

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Stein, S.E. and Brown, R.L., "Estimation of Normal Boiling Points from Group Contributions," J. Chem. Inf. Comp. Sci. 34, 581 (1994).

Stein, S.E., "An Analysis and Optimization of Mass Spectral Library Search Algorithms," Proc. of the 42nd ASMS Conf., Chicago, IL (in press).

Stein, S.E., "Estimating Probabilities of Correct Identification from Results of Mass Spectral Library Searches," J. Am. Soc. Mass Spectrom. 4, 316 (1994).

Stein, S.E. and Scott, D.R., "Optimization and Testing of Mass Spectral Library Search Algorithms for Compound Identification," J. Am. Soc. Mass Spectrom. 5, 859 (1994).

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Tsang, W., "Dioxins and Furans," in Handbook for Waste Incineration, A. Sarofim and M. Pershing, Eds., John Wiley, New York, NY (in press).

Tsang, W. and Cui, J.P, "Hydrogen Atom Attack on Acetone and Dimethylether at High Temperatures," Proc. of the 19th ISSW (in press).

Tsang, W. and Walker, J.A. "Hydrogen Atom Induced Decomposition of Trichloroethylene at High Temperatures," J. Phys. Chem. (in press).

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Westmoreland, P.R., Burgess, D.F.R., Tsang, W., and Zachariah, M.R., "Fluoromethane Chemistry and its Role in Flame Suppression," Proceedings of the 25th Symposium on Combustion (in press).

Zachariah, M.R., and Tsang, W., "Application of Ab Initio Molecular Orbital and Reaction Rate Theories to Nucleation Kinetics," Aerosal Sci. Tech. 19, 499 (1993).

Zachariah, M.R., and Tsang, W., "Theoretical Calculation of Thermochemistry, Energetics and Kinetics of High Temperature $Si_xH_yO_z$ Reactions," J. Phys. Chem. (in press).

Zhang, Z., Padmaja, S., Saini, R.D., Huie, R.E., and Kurylo, M.J., "Reactions of Hydroxyl Radicals with Several Hydrofluorocarbons: The Temperature Dependencies of the Rate Constants for $CHF_2CF_2CH_2F$ (HFC-245ca), $CF_3CHFCHF_2$ (HFC-236ea), CF_3CHFCF_3 (HFC-227ea), and $CF_3CH_2CH_2CF_3$ (HFC-356ffa), J. Phys. Chem. 98, 4312 (1994).

2. Talks

Babushok, V.I., "Simulation Studies of the Influence of Fluorine and Bromine Containing Fire Suppressants on Ignition Behavior," Malon Options Technical Working Conference, Albuquerque, NM, May 4, 1994.

Babushok, V.I., "The Effects of Flame Retardants on Ignition Processes," 25th International Symposium on Combustion, 25th International Symposium on Combustion, Irvine, CA, August 8, 1994.

Buckley, T.J., "Analysis of Errors in Kinetic Flash Photolysis Resonance Fluorescence Experiments," Second Biennial Trombay Symposium on Radiation and Photochemistry, Bombay, India, January, 20, 1994.

Carter, R.W., "Temperature Standards for DSC," High Accuracy, Power Compensated DSC Workshop, Binghamton, NY, July 15, 1994.

Clifton, C., "Problems and Progress in the Measurement of Reference Mass Spectra," 42nd Meeting of the American Society for Mass Spectrometry, Chicago, IL, June 2, 1994.

Domalski, E.S., "Basic Chemistry Research for Industrial Products and Processes," 208th American Chemical Society Meeting, Washington, DC, August 22, 1994. Invited

Fahr, A., "Scatter Light and Accuracy of the Absorption Cross Sections Measurements of Weak Absorptions," NASA/NOAA/AFEAS Workshop on Atmospheric Degradation of HCFCs and CFCs, Boulder, CO, November 17, 1993. Invited

Fahr, A., "Rate Determinations for Vinyl Radical Reactions," Chemical Kinetics and Thermodynamics Seminar, Gaithersburg, MD, February 18, 1994.

Fahr, A., "Ultraviolet Absorption Spectrum of CF_3I, Temperature Dependencies of the UV Cross Sections," Halon Options Technical Conference, Albuquerque, NM, May 3, 1994.

Fahr, A., "Temperature Dependence of the Ultraviolet Absorption Cross Sections of Alternate Halocarbons," Spring Meeting of American Geophysical Union, Baltimore, MD, May 23, 1994.

Fahr, A., "Recent Direct Rate Determination for Vinyl Radical Reactions Pertinent to Planetary Atmospheres," Spring Meeting of American Geophysical Union, Baltimore, MD, May 24, 1994.

Green, D.S., "Nonlinear Laser Spectroscopy for Probing Plasma Chemistry," Meeting of Society of Optical Engineering, Los Angeles, CA, January 28, 1994.

Hudgens, J.W., "New Ways to Optically Detect CH_2 and HCF Radicals Using Resonance Enhanced Multiphoton Ionization Spectroscopy," Symposium on Laser Techniques for

State-Selected and State-to-State Chemistry, 93/SPIE, Los Angeles, CA, January 27, 1994. Invited

Hudgens, J.W., "New Spectroscopy of Free Radicals Produced by the Reaction of Fluorine and Chlorine with Diborane," Symposium on Laser Techniques for State-Selected and State-to-State Chemistry, 94/SPIE, Los Angeles, CA, January 28, 1994.

Hudgens, J.W., "Structure Matters: Detection of Difluoromethyl and Difluoroethyl Radicals by Resonance Enhanced Multiphoton Spectroscopy," 4th Optical Society of America Topical Meeting on Laser Applications to Chemical Analysis, Jackson Hole, WY, March 11, 1994.

Hudgens, J.W., "Observation of Two New Electronic States of the PCl_2 Radical," 49th International Symposium on Molecular Spectroscopy, Ohio State University, Columbus, OH, June 14, 1994.

Hudgens, J.W., "New Electronic States of the CHFCl Radical," 49th International Symposium on Molecular Spectroscopy, Ohio State University, Columbus, OH, June 13, 1994.

Hudgens, J.W., "Detection and Characterization of Group V Dihalides using Multiphoton Ionization," 208th American Chemical Society National Meeting, Washington, DC, August 25, 1994.

Hudgens, J.W., "Multiphoton Ionization Spectroscopy of the CHFCl Radical," 208th American Chemical Society National Meeting, Washington, DC, August 25, 1994.

Hudgens, J.W., "Importance of Chemistry in Non-Thermal Plasma Control of Volatile Organic Compounds and Air Toxics," ELEMCO '94 Meeting, Lubin, Poland, September 8, 1994.

Huie, R.E., "Atmospheric Fate of Halon Alternative Compounds," Aberdeen Proving Grounds, MD, November 3, 1993.

Huie, R.E., "Potential for Further Reactions in the Liquid Phase: Reactions of Haloacetates," NASA/NOAA/AFEAS Workshop on Atmospheric Degradation of HCFCs and HFCs, Boulder, CO, November 18, 1993.

Huie, R.E., "Reactions of Halogenated Peroxyl Radicals," Second Biennial Trombay Symposium on Radiation and Photochemistry, Bombay, India, January 18, 1994.

Huie, R.E., "Reactions of Halogenated Peroxyl Radicals," Indian Institute of Science, Bangalore, India, January 24, 1994.

Huie, R.E., "Free Radical and Photo-Kolbe Reactions," AFEAS Workshop on Decomposition of TFA in the Environment, Washington, DC, February 8, 1994.

Huie, R.E., "Reactions of Halogenated Peroxyl Radicals in Solution," Washington Area Discussion Group on the Chemical Physics of Small Molecules and Free Radicals, Catholic University, Washington, DC, March 8, 1994.

Huie, R.E., "The Atmospheric Chemistry of Iodine Compounds," 208th American Chemical Society National Meeting, Washington, DC, August 25, 1994.

Irikura, K.K., "Thermochemistry of Third-Row Transition Metal Carbene Ions," 15th Annual East Coast Ion Cyclotron Resonance and Ion Molecule Chemistry Symposium, University of Delaware, Newark, DE, October 23, 1993.

Irikura, K.K., "REMPI and Ab Initio Spectroscopy of HCF and DCF," XXIst Informal Conference on Photochemistry, York University, Toronto, Ontario, Canada, May 16, 1994.

Irikura, K.K., "REMPI Spectroscopy of BF_2," 49th International Symposium on Molecular Spectroscopy, Ohio State University, Columbus, OH, June 14, 1994.

Irikura, K.K., "A New Electronic State of BCl," 49th International Symposium on Molecular Spectroscopy, Ohio State University, Columbus, OH, June 14, 1994.

Irikura, K.K., "Structure and Thermochemistry of Sulfur Fluorides SF_n (n = 1-5) and Their Ions SF_n^+ (n = 1-5)," 208th National Meeting of the American Chemical Society, Washington, D.C., August 23, 1994.

Johnson, R.D. III, "Group IIIB Halide Detection by Rensonance Enhanced Multiphoton Ionization Spectroscopy," XXIst Informal Conference on Photochemistry, York University, Toronto, Ontario, Canada, May 16, 1994.

Johnson, R.D. III, "Multiphoton Ionization Diagnostics for Flourinated Ethyl Radicals; Structural Considerations for Difluorethyl Radicals," 49th International Symposium on Molecular Spectroscopy, Ohio State University, Columbus, OH, June 13, 1994.

Johnson, R.D. III, "Rydberg States of B_2 by Resonance Enhanced Multiphoton Ionization Spectroscopy," 49th International Symposium on Molecular Spectroscopy, Ohio State University, Columbus, OH, June 14, 1994.

Johnson, R.D. III, "Excited Electronic States of PF_2", 208th American Chemical Society National Meeting, Washington, DC, August 25, 1994.

Kirklin, D.R., "Combustion Calorimetry and Inorganic Analytical Chemistry," Inorganic Analytical Research Division Seminar, NIST, Gaithersburg, MD, January 11, 1994.

Kirklin, D.R., "Combustion Calorimetry of Advanced Materials for Technology," National Organization of Black Chemists & Chemical Engineers, Atlantic City, NJ, April 4, 1994.

Kurylo, M.J., "Detection and Analysis of Stratospheric Ozone Depletion Using Airborne and Space Based Sensors," Tsukuba Ozone Workshop, Tsukuba, Japan, February 14, 1994. Invited

Kurylo, M.J., "The Network for the Detection of Stratospheric Change: History and Status," Tsukuba Ozone Workshop, Tsukuba, Japan, February 15, 1994. Invited

Kurylo, M.J., "Stratospheric Ozone Depletion: Latest Scientific Findings," Howard University, Washington, DC, February 23, 1994. Invited

Kurylo, M.J., "Detection and Analysis of Stratospheric Ozone Depletion Using Airborne and Space Based Sensors," 21st Informal Conference on Photochemistry, Toronto, Ontario, Canada, May 19, 1994. Invited

Kurylo, M.J., "The Role of the Network for the Detection of Stratospheric Change in the EOS Timeframe," Workshop on the Interface Between NASA's Earth Observing System and Its Research and Analysis Programs, Tysons Corner, VA, July 14, 1994. Invited

Lias, S., "Quality Control in the NIST/EPA/NIH Mass Spectral Database," PITTCON-94, Chicago, IL, March 1, 1994.

Luo, Y., "Homo-and Heterolytic X-C Bond Energies Part II: Heterolytic Bond Energies in Unsaturated Organic Chain Compounds," 42nd American Chemical Society for Mass Spectrometry, Chicago, IL, June 1, 1994.

Luo, Y., "Homo-and Heterolytic X-C Bond Energies III: Heterolytic Bond Energies in Cycloalkyl Compounds," 42nd American Chemical Society for Mass Spectrometry, Chicago, IL, June 1, 1994.

Mallard, G., "Computerized Chemical Databases," Conference on Using Computers in Pharmaceutical Chemistry, South Bend, IN, October 26, 1993.

Manion, J.A., "Kinetic Aspects of the Reaction of Hydrogen Atoms with Halocarbons,"Halon Options Technical Working Conference, Albuquerque, NM, May 4, 1994.

Manion, J.A., "Hydrogen Atom Attack on 1,2-Dichlorotetrafluoroethane," 25th InternationalSymposium on Combustion, Irvine, CA, August 3, 1994.

Manion, J.A., "Mechanisms for the Gas Phase Removal of Fluorine from Organic Molecules," American Chemical Society, Washington, DC, August 24, 1994.

Mautner, M., "Cluster Models of Ion Solvation and Bioenergetics," Chemical Kinetics & Thermodynamics Division, Gaithersburg, MD, November 19, 1993.

Mikaya, A., "Finding and Dealing With Errors in Reference Mass Spectra," Eastern Analytical Symposium, Somerset, NJ, November 11, 1993.

Mikaya, A., "Pyrolysis Gas Chromatography/Mass Spectrometry of Polyvinylsilanes," Sixth Sanibel Conference on Mass Spectrometry, Sanibel, FL, January 13, 1994.

Mikaya, A., "Classification of Errors and Possibilities of Their Elimination in Mass Spectral Database," PITTCON-94, Chicago, IL, March 2, 1994.

Mikaya, A., "Problems and Progress in the Measurement of Reference Mass Spectra," 42nd American Society for Mass Spectrometry Conference, Chicago, IL, June 2, 1994.

Neta, P., "Radiolytic Studies on the Reactions of Porphyrins with Organic Radicals," 18th DOE Solar Photochemistry Research Conference, Tahoe City, CA, June 5, 1994. Invited

Neta, P., "Solvent Effects on Reactions of Radicals," Seminar at the Hahn-Meitner-Institute, Berlin, Germany, June 28, 1994.

Neta, P., "Radiolytic Studies on Cobaloximes and Rhodium and Porphyrins," Seminar at the University of Cologne, Cologne, Germany, June 30, 1994.

Neta, P., "Radiolytic Studies on Rhodium Porphyrins," Seminar at the University of Paris 7, Paris, France, July 5, 1994. Invited

Neta, P., "Solvent Effects on Radical Reactions," Gordon Conference on Radiation Chemistry, Newport, RI, July 21, 1994. Invited

O'Hare, P.A.G., "Combustion Calorimetry with Fluorine as an Oxidant: The Technique and some Recent Results," Carnegie Institute of Washington, Washington, DC, October 4, 1993.

O'Hare, P.A.G., "Thermochemistry and Bonding of Compounds of Groups 14 and 16. New Results and Interpretations," International Union of Pure and Applied Chemistry, Conference on Chemical Thermodynamics, Clermont-Ferrand, France, July 17, 1994.

O'Hare, P.A.G., "Thermochemistry of Gaseous Chalcogenide Molecules of Group 14," 49th Annual Calorimetry Conference, Santa Fe, NM, August 1, 1994.

Orkin, V., "Kinetic Estimation of the Possible Anthropogenic Impact on the Ozone Layer Due to Emission of Br(Cl) Containing Substances," 13th International Symposium on Gas Kinetics, Dublin, Ireland, September 15, 1994.

Orkin, V., "Rate Constants for the Reactions Between Hydroxyl Radicals and Fluorinated Ethers," 13th International Symposium on Gas Kinetics, Dublin, Ireland, September 15, 1994.

Stein, S.E., "Optimization and Testing of Mass Spectral Library Search Algorithms for Compound Identification," PITTCON 94 Conference, Chicago, IL, March 2, 1994.

Stein, S.E., "Accomplishments and Directions of the NIST Mass Spectral Data Program," PITTCON 94 Conference, Chicago, IL, March 2, 1994.

Stein, S.E., "Estimation of Boiling Points of Organic Compounds," Union Carbide Co., Charlestown, WV, May 18, 1994.

Stein, S.E., "Estimation of Boiling Points of Organic Compounds," Dow Chemical Co., Midland, MI, May 19, 1994.

Stein, S.E., "Estimation of Boiling Points of Organic Compounds," Michigan Technology University, Houghton, MI, May 20, 1994.

Stein, S.E., "Building the NIST/EPA/NIH MS Library," 42nd American Society of Mass Spectrometry Conference, Chicago, IL, June 1, 1994.

Stein, S.E., "Identification and Treatment of Errors in the NIST Mass Spectral Database," 42nd Meeting of the American Society for Mass Spectrometry, Chicago, IL, June 2, 1994.

Stein, S.E., "A New Mass Spectral Library Search System," 42nd Meeting of the American Society for Mass Spectrometry, Chicago, IL, June 3, 1994.

Tsang, W., "The High Temperature Decomposition and Formation of Toluene," 1993 Technical Meeting of the Eastern States Section of the Combustion Institute, Princeton, NJ, October 25, 1993.

Tsang, W., "Data Evaluation and Prediction in Support of Halon Project," Program Review, Army Research Laboratory, Aberdeen Proving Ground, MD, November 4, 1993.

Tsang, W., "Single Pulse Shock Tube Studies on the Unimolecular Decomposition of Large Unsaturated Molecules: Trans-1-Phenyl-1-Pentene," Combustion and Soot Formation Symposium, American Chemical Society National Meeting, San Diego, CA, March 14, 1994.

Tsang, W., "High Temperature Methods for the Destruction of Chemical Agents,"NATO Advanced Workshop on Destruction of Military Toxic Materials, Naaldlwijk, The Netherlands, May 19, 1994. Invited

Tsang, W., "Comments on Draft of the Combustion Emissions Technical Resource Document," Environmental Engineering Committee, Science Advisory Board, USEPA, Washington, DC, June 15, 1994. Invited

Tsang, W., "Hydrogen Atom Attack on 1-Phenylpropene at High Temperatures," 25th International Symposium on Combustion, Irvine, CA, August 6, 1994.

Tsang, W., "Reactions of Hydrogen Atoms with Organic Compounds at High Temperatures," Hydrogen Transfer in Hydrocarbon Processing Symposium, National American Chemical Society Meeting, Washington, DC, August 25, 1994. Invited

Tsang, W., "High Temperature Multichannel Decomposition of Methane and Ethane," 13th International Symposium on Gas Kinetics, Dublin, Ireland, September 15, 1994.

Tomaszkiewicz, I., "Standard Molar Enthalpies of Formation of Tungsten (W_5Si_3) and Molybdenum (Mo_5Si_3) Silicides," 49th Annual Calorimetry Conference, Santa Fe, NM, August 2, 1994.

3. Cooperative Research and Development Agreements (CRADAs)

The Development of an Advanced Mass Spec Searching System, S.E. Stein
Bio-Rad Laboratories, Inc., Sadtler Division (CRADA)

4. Patent Awards and Applications

None

5. SRM Activities

SRM 2683a	Calorific Value and Sulfur in Coal (Updated)
SRM 2684a	Calorific Value and Sulfur in Coal (Updated)
SRM 2776	Calorific Value and Sulfur in Coke (Certified)

6. SRD Activities

SRD 1	NIST/EPA/NIH Mass Spectral Database (DLL Version 1.0)
SRD 17	NIST Chemical Kinetics Database (Version 5.0)
SRD 18	THERM/EST Database (Version 5.2)
SRD 25	NIST Structure and Properties Database (Version 2.0)
SRD 40	NDRL/NIST Liquid Phase Kinetics Database (Version 2.0)
SRD 44	DIPPR Project 861, Aqueous Electrolyte Solution Database

7. Calibrations

None

8. Committee Assignments

E.S. Domalski

1995 Calorimetry Conference (Chairman)
DIPPR Data Compilation Project 801

R.F. Hampson

NASA Panel for Data Evaluation
IUPAC Subcommittee on Gas Kinetics Data Evaluation for Atmospheric Chemistry (Secretary)

H.E. Huie

American Working Group in Physical and Material Sciences of the Indo-US Subcommission on Science and Technology
IUPAC Subcommittee on Aqueous Kinetics Data Evaluation for Atmospheric Chemistry (co-chairman)

D.R. Kirklin

ASTM E-34 Committee on Waste Management

M.J. Kurylo

NASA Panel for Data Evaluation
International Scientific Steering Committee, Network for the Detection of Stratospheric Change (Chairman)
NASA Atmospheric Effects of Aviation Project, Advisory Panel

S.G. Lias

ASTM E-49 Committee on Computerization of Material Property and Chemical Data
American Society for Mass Spectrometry, Measurements and Standards Committee
American Society for Mass Spectrometry, Nominating Committee
American Society for Mass Spectrometry, Board Member for Standards and Measurements
Organizing Committee of Sanibel Conference

W.G. Mallard

ASTM E-49 Committee on Computerization of Material Property and Chemical Data
NIST/EPA/NIH Mass Spectral Database, Steering Committee
Joint Committee on Atomic and Molecular Physical Data

D.B. Neumann

ASME Research and Technology Committee on Properties of Water and Steam in Thermal Power Systems

P.A.G. O'Hare

IUPAC Commission on Thermodynamics

S.E. Stein
American Chemical Society, Computers in Chemistry Division, Alternate Councilor

W. Tsang
JANNAF Panel on Kinetic and Related Aspects of Propellant Chemistry
Third International Conference on Chemical Kinetics, Review Committee

9. Editorships

M.J. Kurylo
International Journal of Chemical Kinetics (Chemistry Board)

S.G. Lias
Organic SEARCH (Structure, Energies and Reactivity in Chemistry) Series (Chapman and Hall)

P. Neta
Radiation Physics and Chemistry (Chemistry Editor)

P.A.G. O'Hare
The Journal of Chemical Thermodynamics (Editor)
Solution Calorimetry (Blackwells) (co-editor)
NIST Journal of Research (Editorial Board)

S.E. Stein
ACS Chemputer Guide (Editorial Board)

W. Tsang
Journal of Physical and Chemical Reference Data (Editorial Board)

10. Seminars

October 18, 1993
V.D. Knyazev, Dept. of Chemistry, Catholic University of America, Washington, DC, "Chemistry of the Chloroethyl Radical." (Division Sponsor: W. Tsang)

October 22, 1993
M.S. Chandrasekharaiah, HARC, Materials Science Research Center, The Woodlands, TX, "Spot Method for Measuring the Liquidus and Solidus Boundaries of Binary Phase Systems with High-Melting Components." (Division Sponsor: P. O'Hare)

October 24, 1993

M.S. El-Shall, Dept. of Chemistry, Virginia Commonwealth University, VA, "New Approaches to Cationic Polymerization in the Gas and Condensed Phases." (Division Sponsor: L.W. Sieck)

December 8, 1993

Y.M. Molin, Institute of Chemical Physics, Novosibirsk, Russia, "Quantum Oscillations in Recombination of Radical-Ion Pairs Under Radiolysis of Liquid Solutions." (Division Sponsor: W. Tsang)

January 28, 1994

A. Korol, Arvada, CO, "Evaluation of GC Retention Data." (Division Sponsor: S. Stein)

February 2, 1994

B. Yang, Dalian Institute of Physics, P.R. China, "Expert Systems for Mass Spectral Interpretation." (Division Sponsor: S. Stein)

February 7, 1994

V.G. Zaikin, Institute of Petrochemical, Synthesis of Russian Academy of Science, Moscow, Russia, "Stereochemistry and Mass Spectrometry." (Division Sponsor: S. Stein)

March 18, 1994

B. Wladkowski, Biotechnology Division (CARB), NIST, "Energetics and Dynamics of Gas-Phase S_N2 Reactions." (Division Sponsor: K. Irikura)

March 21, 1994

M.F. Tuckler, School of Chemical Sciences, University of Illinois at Urbana, Urbana, IL, "Direct Observation of Bimolecular Processes: The Time Resolved Study of BrI_2 Complexes Formed From $HBr-I_2$ Van der Waals Molecules." (Division Sponsor: J. Hudgens)

April 20, 1994

L.A. Curtiss, Argonne National Laboratory, Argonne, IL, "Evaluation of Bond Energies, and Electron Affinities to Chemical Accuracy Using Quantum Chemical Methods." (Division Sponsor: P. O'Hare)

May 20, 1994

H. Levanon, Hebrew University of Jerusalem, Jerusalem, Israel, "The Dynamics of Photoexcited Fullerenes." (Division Sponsor: P. Neta)

May 26, 1994

J.P. Mittal, Bhabha Atomic Research Centre, Trombay, Bombay, India, "Pulse Radiolysis and Flash Photolysis Studies at BARC." (Division Sponsor: P. Neta)

11. Conferences/Workshops/Sessions Sponsored/Co-Sponsored

August 1-5, 1994

49th Annual Calorimetry Conference, Santa Fe, NM (E.S. Domalski)

August 25, 1994

American Chemical Society Symposium on "Advances in Replacements for Ozone Depleting Compounds, Halon Replacements: Technology and Science," Washington, DC (A. Miziolek and W. Tsang)

12. Cooperative Research Agreements

Professor Joel F. Liebman, University of Maryland Baltimore County, "Thermochemical Properties of Organic Chemicals: Information Collection and Development of Estimation Schemes"

Dr. David S. Green, Stanford University, "Using Degenerate Four-Wave Mixing for Remote Measurements of Chemical Processes"

Dr. Houston Miller, George Washington University, "Development of an Expert System for Predicting Kinetic and Thermodynamic Properties of Molecules"

III. Inorganic Analytical Research Division (834)

William F. Koch, Chief

A. Division Overview

The Inorganic Analytical Research Division (IARD) serves as the Nation's Reference Laboratory for inorganic chemical analysis and metrology to enhance U.S. industry's productivity and competitiveness, assure equity in trade, and improve public health, safety, and environmental quality. The Division conducts research and development on the accurate quantitative measurement of the inorganic chemical composition of materials. These efforts include the development and dissemination of advanced analytical methods, instrumentation, and reference materials, and the study of the fundamental and underlying principles of the chemical processes and reactions involved in chemical analyses. IARD provides these infrastructural capabilities for the Nation - U.S. industry, government agencies, and the academic and scientific communities. The Division is aligned according to discipline and consists of four groups: Atomic and Molecular Spectrometry, Electroanalytical Research, Mass Spectrometry, and Nuclear Methods. A realignment within the Division was effected in FY94, moving the classical chemistry component of the Atomic and Molecular Spectrometry Group to the Electroanalytical Group. This strategic shift focuses the high-accuracy, fundamental, physico-chemical analytical methods, providing critical mass, and emphasizing the critical role of chemical metrology in addressing industrial needs.

IARD remains responsive to the needs of its constituencies through numerous type of interactions and outputs. Complementing our permanent staff of 46 scientists and engineers, 32 guest scientists conducted research and made measurements in our laboratories. In addition, we continue to provide specialized chemical analyses for other organizations both within and outside of NIST. For example, this past year we developed procedures for the accurate assay of tungsten silicide, an important high technology material for semiconductors. Knowledge of the exact stoichiometry of this, as well as related materials, is critical to determining the thermodynamic properties necessary for modelling and predicting performance and suitability.

In FY94, the Division issued 317 Reports of Analysis and Reports of Recertification, primarily in keeping with our strong commitment to the Standard Reference Materials Program. These reports covered over 90 Standard Reference Materials. This past year we have continued our effort to conform to the international guidelines for reporting measurement results. This conformance brings into harmony chemical and physical metrological practice. The thorough examination of all sources of error in the totality of the chemical analysis has resulted in a better understanding of the measurement process, and pointed the way for advancing the science. The Division's highly motivated staff produced over 90 publications and presented 70 talks to scientific audiences around the world. In addition, there were 8 active Cooperative Research and Development Agreements (CRADAs), as well as one patent issued, in IARD in FY94. Over half of our technical staff actively participates in outside standards committees and activities, including ASTM, IUPAC, and NCCLS. The Division sponsored 3 workshops in FY94 involving secondary reference materials for lead, sustainable development, and international chemical metrology. A summary of some of the outstanding activities of the Division follows, aligned along the CSTL Thrust areas, with expansion of the major accomplishments provided in the Technical Highlights.

Fundamental Measurement Technology. The Division demonstrated its worldwide leadership role in high accuracy chemical metrology by chairing the CIPM working group responsible for conducting an international interlaboratory chemical analysis of selected metals in solution. Using isotope dilution mass spectrometry, the Mass Spectrometry Group benchmarked other national laboratories around the world and is developing the detailed protocol for the next phase of this project. The Group has also advanced the capabilities of inductively coupled mass spectrometry (ICP-MS), which is becoming the technique of choice in analytical instrumental laboratories, by investigating chemical procedures for minimizing ICP-MS memory and sample cross contamination. Continuing their efforts in refining the definitive methodology of isotope dilution mass spectrometry, the scientists in this Group have modified the NIST thermal ionization instrument for either Faraday cup or high sensitivity pulse counting detection, and have investigated negative thermal ionization procedures for Os/Re geochemical studies. Taking advantage of the world-class cold neutron research facility (CNRF) at NIST, the Nuclear Methods Group has directed a significant part of their overall effort on the analytical applications of cold neutrons. The project on the focussing of neutrons in collaboration with X-ray Optical Systems, Inc. (a recipient of a NIST Advanced Technology Program, ATP award) and the Kurchatov Institute in Moscow, realized a major breakthrough in neutron focussing. Fundamental studies continued on the evaluation of the physical basis for neutron transmission through polycapillary fibers. The Nuclear Methods Group improved the cold neutron prompt gamma activation analysis (CNPGAA) facility by installing a helium purgeable, vacuum-tight sample chamber, setting up and testing a BGO Compton suppressor, and evaluating anti-cosmic ray shielding for reducing gamma-radiation background. The Group also furthered its investigation in the use of focused neutrons for CNPGAA, exploring the parameters for measuring trace hydrogen in advanced materials and characterizing the effects of target cooling and neutron scattering.

The Electroanalytical Research Group, continuing its research in the development in much-needed standards for electrolytic conductivity measurements, has developed low electrolytic conductivity reference materials that can be used to calibrate water purity in power plants. Research continued on the development of absolute DC conductimetric metrology based on primary electrical and length standards. Active collaborative research was maintained with the Office of National Measures in Hungary, and initiated with the Danish Institute for Fundamental Metrology. Maintaining its world leadership in high accuracy analyses, the Group has advanced the science of coulometry used to determine the purity and stoichiometry of the elements and compounds on an absolute basis by fully automating the system. Further promulgating the NIST system of pH standardization, we have established formal collaborative efforts with the Office of National Measures in Hungary and the recently established national laboratory for pH in Denmark. Future plans include the development of Ph standards in nonaqueous-aqueous solvents necessary for alcohol-based fuels and for medical applications in cryogenics.

The Fourier transform UV/VIS spectrometer is being used by the Atomic and Molecular Spectrometry Group in collaboration with Iowa State University to generate an ICP-OES wavelength reference atlas. This year the group began to measure ICP wavelengths with 3 parts in 10^7 accuracy for this new atlas. A novel procedure has been developed for macro-scale elemental compositional mapping of metals. The system uses a glow discharge optical emission source coupled to a Hadamard Spectrometer. Data for preliminary test samples have proven in principal that compositional mapping can be accomplished with 4-mm resolution. Optimized transfer and integrating optics are now being designed. To improve the quality of one of the very important classes of SRMs maintained in the Division, we have developed a CCD camera-based method for evaluating the transmittance uniformity of candidate SRM optical filter materials. In other cutting edge research, the Division has performed preliminary measurements to evaluate an isotope dilution optical emission spectrometric (ID-OES) approach for accurate analyses, developed a chemometric approach for choosing optimum internal standard elements and spectral lines using an array detector ICP spectrometer system, measured significant laser-enhanced ionization in a standard chemical flame using mass spectrometric detection, and developed a quantitative fundamental parameter procedure for the analysis of flat geological specimens using x-ray microfluorescence spectrometry.

Process Technologies. The Division supports advances in the broad field of process technologies through the application of basic research in analytical metrology to measurements and standards for on-line monitoring, materials characterization, and methods development. It has long been recognized that a problem with high temperature alloys is their sensitivity to embrittlement caused by the presence of hydrogen. Our measurements of hydrogen in turbine blades using CNPGAA indicated an elevated hydrogen concentration in the regions of failure. We have also determined H/Ti ratios in cross sectional slices of jet engine compressor blades. Using cold-neutron depth profiling (CNDP) techniques pioneered at NIST, we have measured ^{17}O profiles in Ta_2O_5, and made annealing studies of boron in CVD-diamond. In a study essential to the semiconductor industry, the data collection for an ASTM-sponsored international comparison of high-purity silicon has been completed. Working with the U.S auto industry, we have consummated a CRADA to transfer ICP-MS measurement methodology for the determination of precious metals in automobile catalysts. Accurate assays of Pt, Pd, and Rh are critical to the industry that estimates usage at approximately $500 million per year.

On-line analyzers which measure near infra-red (NIR) spectral features of process streams are increasingly being used to optimize and control chemical processes in industry. We have begun a cooperative effort with the Center for Process Analytical Chemistry (CPAC) to develop wavelength and intensity standards for NIR spectrophotometry. The ultimate goal is to be able to provide field analyzers with a common calibration function.

Environmental Technology. A long-standing priority of all the Groups in the Division has been analytical measurements and standards in support of environmental issues. This year we have become involved in a major new program initiative of the US EPA, the National Human Exposure Assessment Survey (NHEXAS), providing quality assurance and measurement traceability. In addition, NIST and the U.S. Environmental Protection Agency have been working together to provide real-world reference materials of paint, soil, and dust for benchmarking the accuracy of analytical methods and for evaluating inter-laboratory performance and quality assurance activities. Increasing interest in identifying environmental sources of lead poisoning has prompted the need for rapid and accurate analytical methods. This year we have developed a slurry sample introduction electrothermal atomic absorption spectroscopy (AAS) method for rapid evaluation of environmental samples for lead contamination, continued the development of new Pb in powdered paint and dust SRMs, developed EPA/NIST Research Materials for evaluation of portable XRF analyzers and chemical test kits, and initiated homogeneity testing of lead-doped tibia bone phantoms as an SRM for in-vivo lead-in-bone measurements. We have also examined variables in the EPA leaching method applied to paint in order to optimize analytical conditions to ensure measurement consistency and comparability.

The accurate assessment of mercury is another environmental challenge facing the United States. To meet this need, scientists in the Nuclear Methods Group have re-established and improved the combustion method for mercury by Radiochemical Neutron Activation (RNAA). Expanding the applications of isotope dilution ICP-MS, the Mass Spectrometry Group has developed an advanced method for Hg and used it on SRM 1641c, Hg in water. Other important environmental SRMs actively engaged in by the Division in FY94 include whale blubber, marine mammal livers, industrial and municipal sludge, drinking and natural water, coals, and fuel oils.

Health Care Technology. The Division has taken an active role in identifying and responding to the measurement and quality assurance needs of the clinical community. Several Division scientists participate on various committees of the National Committee for Clinical Laboratory Standards, including those involving electrolytes, trace metals, and Ph. This year the College of American Pathologists (CAP) continued its support for the Reference Laboratory for Clinical Analysis within the Inorganic Analytical Research Division through the Research Associate Program. This program, formalized by a CRADA between CAP and NIST, focuses on the development of reference methods for analytes of interest to clinical chemistry and to provide accurate analyses of reference, survey and challenge materials for the nationwide CAP studies. In FY94, the research effort developed methods for determination of Ca and Na in clinical materials using ICP-MS. It is likely that this work will become the basis for new Reference Methods for these analytes, replacing the flame methods currently in use. Accurate analytical methods for the speciation of iron will be a high priority in next year's program.

Chromium plays an important role in biological processes. It is essential for glucose and lipid metabolism in both plants and animals, yet in certain forms chromium is toxic at levels that are only a few orders of magnitude higher than are nutritionally required. For many analytical techniques, chemical dissolution or fusion is the first step in the analytical procedure. However, losses of chromium during the dissolution process are a problem in the analysis of botanical materials. This year the Division mounted a major effort to determine optimum conditions for the complete dissolution of botanical materials without loss of chromium, employing the unique capabilities of INAA to track chromium throughout the procedure.

Awards and Recognition. The high caliber of the Division's scientific staff has been duly recognized as evidenced by numerous awards bestowed this year. Ellyn Beary and Paul Paulsen received the NIST Bronze Medal for their contributions to the advancement of isotope dilution inductively coupled plasma mass spectrometric methods used for high-accuracy and ultratrace chemical analyses in materials ranging from industrially important optical fibers and automobile catalysts to environmentally relevant samples, such as soils and sludge, and used to establish a baseline for international standards activities in chemical analysis. Also receiving NIST Bronze

Medals were Drs. Heather Chen-Mayer, Greg Downing, and David Mildner for their development of theoretical concepts regarding the physics and mathematics of neutron optics. Their effort led to the development of glass-capillary lenses capable of focusing neutrons for analytical applications and demonstrated the capability to guide and focus neutron beams using polycapillary fibers. The coveted Edward Uhler Condon Award, which recognizes distinguished achievement in written exposition in science and technology, was bestowed on Charles M. Beck, II. Mr. Beck was recognized for his landmark paper entitled "Classical Analysis, A Look at the Past, Present, and Future" which traces the history of classical chemical analysis from the mid 1600s and demonstrates that classical analysis remains essential for accurately determining major and minor constituents and establishing primary standards for calibration based instrumental analysis, and is vital to the interests of U.S. industry. Three members of the Division, Kenneth Pratt, Donald Becker, and Charles Beck, received Measurement Services Awards for their continuing outstanding contributions to the Standard Reference Materials Program. Drs. Paul Paulsen and Jack Fassett were the Division's nominees for the CSTL Technical Achievement Award for their benchmarking metrological efforts in the analysis of automobile catalysts.

Future Directions. With the purpose of consolidating and focussing analytical research and measurement, the Chemical Science and Technology Laboratory will combine IARD with the Organic Analytical Research Division to form the new Analytical Research Division (839) in FY 1995. The core of the IARD will continue its leadership role in advanced analytical method research and development critical to the needs of U.S. industry and in support of other government agencies, especially in the areas of quality assurance, environmental technologies, clinical chemistry, and advanced materials and manufacturing. These efforts will include the development and certification of reference materials essential to our broad analytical constituency, as well as to emerging technologies, providing the chemical measurement infrastructure for the nation. Responding to the realities of the global marketplace, we will expand our international collaborations and intercomparisons. The synergism created by the combination of the two divisions will support and enhance these efforts.

B. Selected Technical Reports (Inorganic Analytical Research Division)

1. Investigation of Isotope Dilution Mass Spectrometry as a Basis for International Comparability of Chemical Measurements

E.S. Beary, J.D. Fassett, P.J. Paulsen, M.S. Rearick, R.D. Vocke, and R.L. Watters, Jr.

The problem of providing uniformity and traceability in chemical measurements is an issue of major international and national concern. A Working Group on Metrology in Chemical Measurement of the International Committee of Weights and Measures (CIPM) was organized to examine this issue and proposed an exploratory program of cooperative work among leading national metrology laboratories. One of the initial projects recommended was an interlaboratory comparison of a relatively simple matrix using isotope dilution mass spectrometry (IDMS). The hypothesis is that coordinated activity on the analysis of a few key reference materials, using one or two reference methods of wide application, will provide a base from which to extend international comparability to a wider range of methods and reference materials.

IDMS was chosen as the reference method because its inaccuracies and imprecisions have been proven to be relatively small and it is used within some national traceability networks to evaluate the accuracy of other chemical methods. NIST has used IDMS extensively in the certification of its Standard Reference Materials (SRMs). The Inorganic Analytical Research Division took the lead in designing the IDMS interlaboratory project, coordinated the preparation and distribution of the unknown samples, and provided the separated stable isotopes required for IDMS. In addition, the samples were analyzed (blind) in the Mass Spectrometry Group using inductively coupled plasma (ICP-MS) and thermal ionization (TIMS) mass spectrometry.

The target level of error and uncertainty for the analytical measurements was established by the Working Group at one percent relative. Between 6 and 9 laboratories submitted results using IDMS for the six analytes for a total of 46 IDMS elemental determinations. The mean of only 24 of these determinations fell within the target limits (52%). Only two laboratories submitted results that were within the target uncertainties for all analytes, representing half of the total. NIST was one of these laboratories. Only 9 of the 46 reported results showed measurement precision of 0.10 % or better which is representative of the state-of-the-art for IDMS.

The conclusion of this initial exercise is that neither the inherent accuracy or precision of the IDMS technique were consistently realized by most of the laboratories, in general caused by the lack of experience with this technique. The dispersion of results is typical of the first round of an interlaboratory study and underscores the need for traceability systems to be established. NIST will participate in documenting and disseminating the IDMS protocol that results in accurate measurement. Once the protocol has been reviewed and accepted, a second analysis round will be undertaken. Ultimately, cooperative action by the national metrology laboratories should lead to analytical improvements and comparability for increasingly demanding chemical measurements.

2. Assay of Tungsten Silicide for the Accurate Determination of Its Standard Molar Enthalpy of Formation

C.M. Beck

The interest in the thermodynamic properties of W_5Si_3 stems from its prominence in a number of modern industries. W_5Si_3, and, therefore, its thermodynamic properties, are important in: the chemical vapor deposition (CVD) of W in VLSI (very large scale integration) applications; the formation of single-phase W_5Si_3 as a gate electrode on GaAs substrates in integrated circuits; the role of W_5Si_3 in the formation of thin-film tungsten silicide and its deposition on (silica + silicon) substrates; and the use of W_5Si_3 along with SiC in the production of composites.

Although specific enthalpies of reaction of substances like W_5Si_3 can be measured with precision using fluorine-bomb calorimetry, conversion of these results to a reliable standard molar enthalpy of formation requires an accurate assay of the substance. After several unsuccessful attempts, the following analytical technique was devised to assay W_5Si_3. For the Si assay, accurately-weighed specimens contained in quartz boats were oxidized for 12 h in a muffle furnace at a temperature of 780 °C, thus converting the starting material to a mixture of WO_3 and SiO_2. Afterwards, the quartz boat and its contents were heated in a tube furnace to 800 °C in a flow of Cl_2 gas for 12 h. This treatment converted the WO_3 to volatile tungsten oxychloride. X-ray analysis of the resulting SiO_2 revealed a small amount of WO_3 contaminant. The SiO_2 together with the WO_3 impurity was transferred to a Pt crucible and the SiO_2 was dissolved in HF and volatilized as SiF_4. The weight of the WO_3 was determined by difference, and the %Si in the original sample was calculated.

For the W assay, accurately-weighed specimens contained in Pt crucibles were carefully dissolved by covering them with HNO_3 and adding HF dropwise. Cautious evaporation of the resulting solution removed the silicon as SiF_4, while the HNO_3 oxidized the tungsten to the hexavalent state. Subsequent ignition of the crucible on a hotplate, and then in a muffle furnace at 780 °C for 1 h produced dry WO_3, which was shown by X-ray fluorescence to be free of trace impurities below one part in 10,000. The weight of WO_3 was used to calculate the %W in the starting material. The two specimens of W_5Si_3 assayed turned out to be $W_5Si_{2.96}$ and $W_5Si_{3.11}$. This is within experimental agreement with the most recent phase-diagram assessments which give a composition range of W_5Si_3 to $W_5Si_{3.33}$. In fiscal 1995, in addition to completing the work on Mo_5Si_3, we plan to assay SiS_2 and $MoTe_2$.

3. Reference Measurements for Platinum Group Elements in Automobile Catalysts Using ICP-MS

E.S.Beary and P.J. Paulsen

Catalytic converters have been standard equipment on automobiles since the 1970s when the first controls on exhaust emissions were imposed. These devices are used to convert CO and hydrocarbons to CO_2 and NOx to nitrogen and water. The active components of automobile catalysts are the elements platinum, palladium, and rhodium, whose costs/g are comparable to gold. Automobile catalysts are a principle use for these elements; the industry uses on the order of $500M worth of platinum group elements per year. The automobile industry is actively studying ways to increase the efficiency of catalytic converters and reduce their cost. In addition, recovering the precious metals in catalysts is an expanding industrial activity.

We have recently developed and applied methods for determination of the platinum group metals in automobile catalysts using inductively coupled plasma mass spectrometry. The determination of Pt and Pd relied on the known high accuracy of isotope dilution analysis. The quantification of the mononuclidic element Rh required a combination of internal and external calibrations and careful assessment of potential systematic errors. These potential errors could result from instrumental interferences, as well as problems in solubilization. Matrix matching was done to ensure interference-free Rh measurement; dissolution was done using the high temperatures and pressures of the Carius tube method.

Two revert (used) autocatalyst materials were certified for their platinum group content at the request of the International Precious Metals Institute (IPMI). These standards were requested because of the large between-laboratory differences in results achieved by the IPMI members. NIST was asked to provide materials with 1 % relative uncertainty or better for the elements Pt, Pd, and Rh, and this need was subsequently met by applying the ICP-MS methods.

An indirect result of this work was the invitation to an industrial workshop on improving the measurement capabilities of industry for new autocatalyst materials. A CRADA has been established whose goal is to demonstrate the transferability of NIST IDMS and reference measurement methodology directly to the industrial laboratory. New autocatalyst material is being examined whose composition presents different and, in some ways, an easier analytical challenge. The autocatalyst SRMs will be invaluable in the validation of this methodology transfer and, perhaps, the development of new methodology.

4. A dc Method for the Absolute Determination of Conductivity of Primary Standard KCl Solutions from 0 to 50 °C

Y.C. Wu

Electrolytic conductivity is determined by the resistance of a test solution in a conductivity cell with two electrodes. The effective distance between the two electrodes divided by the effective diameter of the tube is called the cell constant of the given cell. The cell constant is determined either by geometrical means or by calibration with a standard of known conductivity. The general practice adopted internationally is the use of calibration. Therefore, the primary conductivity standard solutions become of utmost importance.

A set of old primary conductivity standards of KCl solutions exists with values for limited temperatures (0, 18, and 25 °C). These were determined in 1933 and three "demal" units (1D, 0.1D, and 0.01D) were created. The "demal" is defined by the mass of KCl per kg of aqueous solution: 71.1352, 7.41913, and 0.745263 g KCl per kg solutions for 1D, 0.1D, and 0.01D KCl, respectively. These units are illogical, cumbersome, and most definitely, non-SI. Furthermore, the temperature range is limited. For these reasons we have not only verified the conductivities for 0.1 and 0.01 demal solutions but also determined conductivities for the 0.1 and 0.01 molal (mol KCl/kg H_2O) KCl solutions in the temperature range of 0 to 50 °C in five-degree intervals with the ac absolute method published previously.

The conductivity values for the 1D and 1 molal KCl solutions have not been done with the same setup because the cell constant is too small and the lead resistance correction becomes significant. We have decided to use a dc absolute method for these high-conductance solutions. It is a four-terminal cell with four electrodes, two for current and two for potential. This eliminates the lead resistance correction in the measurement. The new feature is that the section for potential measurement is removable so that its dimension can be measured mechanically with high precision. The conductivities for 1D and 1 molal KCl solutions in the temperature range from 0 to 50 °C in five-degree intervals have been determined this year. This set of data, together with values previously determined by the ac method, will be submitted to OIML and IUPAC for adoption as the international primary conductivity standards.

In FY95, we plan to determine the electrolytic conductivity for proposed future primary standard KCl solutions of higher and lower molalities, i.e., $m_{KCl} > 1.0$ molal and $m_{KCl} < 0.01$ molal, needed to fill the gap required by laboratories.

5. Low Electrolytic Conductivity Standards for Industrial Applications

Y.C. Wu and P.A. Berezansky

Conductimetric monitoring and control of the quality of feedwater and boiler water are necessary for power plants. Conductivity is used as a measure of ionic contaminants in water. The generation of steam at high temperature and pressure requires that contaminants be strictly limited to very low levels to prevent corrosion and scaling. The theoretical value for the conductivity of pure water at 25 °C is 0.055 μS cm^{-1}. The absorption of ambient carbon dioxide by pure water can cause the conductivity to increase to approximately 1 μS cm^{-1}. This value varies with the carbon dioxide content in the atmosphere. If the water is contaminated with a minute amount of ionic substance, for example, 1 μg g^{-1} calcium chloride, the conductivity increases to about 3 μS cm^{-1}. In order to assure the purity of this water, conductivity standards below 30 μS cm^{-1} are necessary to provide conductivity measurements of sufficient accuracy.

A new NIST standard reference material (SRM) for low electrolytic conductivity, SRM 3199, has been prepared from potassium chloride in a 30% n-propanol-water mixture with an electrolytic conductivity of 15 μS cm^{-1}. In this mixed solvent, the absorption of ambient carbon dioxide contributes less than 0.1 μS cm^{-1} to the solvent conductivity and hence does not vary significantly. This decreases the uncertainty of these standards compared to standards of similar conductivity prepared using pure water. The electrolytic conductivity of solutions of potassium chloride and benzoic acid in 30% n-propanol-water was determined as a function of concentration. Based on this data, users are able to prepare standards at 5, 10, 15, 20, and 25 μS cm^{-1} for use in cell calibration and quality control.

A second SRM for low electrolytic conductivity, prepared from potassium chloride in 30% n-propanol-water, with an electrolytic conductivity of 5 μS cm^{-1} will be released in FY95. During FY95, the conductivity of these standards will be closely monitored to insure their stability.

6. Practical Wavelength Calibration Considerations for UV-Vis FTS

M.L. Salit, J.C. Travis, and M.R. Winchester

The inductively coupled plasma (ICP) is widely employed as a source for chemical analysis using atomic emission spectroscopy. One estimate predicts more than 11500 ICP instruments installed worldwide by the end of 1994. A principal source of error in ICP measurements arises from spectral interferences and line mis-identification. To help alleviate errors in these measurements, a spectral atlas idiosyncratic to the ICP is being compiled to provide the necessary reference data for accurate line identification and interference prediction. NIST has unique Fourier transform spectroscopy (FTS) instrumentation, giving us the capability to accurately determine wavelengths in spectral sources. A design goal for this atlas is to provide the user with wavelengths with uncertainties on the order of several parts in 10^7.

Wavelength accuracy is a key characteristic of FTS, and impressive results are available with relative ease. Assuming adequate signal-to-noise ratio, wavelength uncertainty arises from two primary phenomena — the effect of using a finite size aperture (and photon detector), and from cosine errors arising from imperfect alignment of the sample and reference beams. These effects are typically small enough to ensure uncalibrated accuracy of about 1 part in 10^5. Significant improvement can be attained through a single point, multiplicative calibration approach, which has been reported to reduce uncertainties to several parts in 10^8. In fact, relative line positions for strong lines within a given spectrum can be determined with a precision of several parts in 10^9.

Though it is most appropriate to employ a wavelength standard *in the source* as the calibration reference, there are situtations in which this is either inconvenient or impossible — our ICP atlas, for example. External calibration offers flexibility in selecting the standard and the conditions under which it is used. If the calibration source and the sample source can be arranged so as to illuminate the aperture identically, even the source geometry of the calibration source is irrelevant. We have developed an approach to unambiguously achieve such arrangement, making the accurate use of an external calibrant practical. An integrating sphere is employed to either mix light from a wavelength standard and a sample in the same spectrum, or to allow sequential spectra of the standard and sample to be obtained.

The role of the FTS in this strategy is to measure a large number of line positions with uncertainties on the order of 1 part in 10^7, which we propose to achieve by "bootstrapping" a small number of better-known ICP transfer standards. These transfer standards will be required to have uncertainties on the order of 5 parts in 10^8. The transfer standards will be determined by mixing a trusted standard in the integrating sphere with the strongest lines from selected elements in the ICP. Experience with electrodeless discharge lamps of ^{198}Hg for calibration of the FTS in the desired wavelength region has been favorable, and there are well trusted wavelengths for this source. Integrating sphere-imaged spectra of both iron in the ICP and ^{198}Hg in the electrodeless lamp have been measured and meet the signal-to-noise criteria required for the atlas work. Activities over the upcoming year will center on instrument alignment to alleviate a line-shape artifact and determination of the ICP transfer standard line positions.

7. Development of Sample Preparation Procedures for Improving the Accuracy of X-Ray Fluorescence Analysis of Lead in Paint, Soil, and Dust

P.A. Pella and A.F. Marlow

Increasing interest in identifying environmental sources of lead poisoning has prompted the need for rapid and accurate analytical methods. Main sources of lead poisoning especially for young children are old paint, soil, and household dust localized in or around homes. NIST and the U.S. Environmental Protection Agency (USEPA) have been working together to provide real-world reference materials of paint, soil, and dust for benchmarking the accuracy of analytical methods and for evaluating inter-laboratory performance and routine quality assurance/control activities. X-ray fluorescence (XRF) spectrometry, one of several methods currently used for such analyses, is rapid, non-destructive, and has sufficient sensitivity for measuring lead-based paint, and lead-containing soil and dust.

In a USEPA study, a protocol for production of homogeneous evaluation materials consisting of powdered paint, soil, and dust samples was tested. An analysis of several of these materials was carried out by round-robin in which a number of laboratories using various analytical methods were used. Significantly low values for lead in paint and dust samples were obtained by the XRF laboratories as compared to the results obtained by laboratories using other analytical methods.

For improving sample preparation for paints in which the lead concentrations are relatively high (e.g., >1%), several methods were tested at NIST prior to XRF analysis. Since it was important to retain the rapid analysis features of XRF, only physical methods of sample preparation were investigated. These consisted of either grinding the material as received in a commercial ball mill or grinding an aliquot of the sample in a ball mill together with sodium carbonate. It was found that for some paint materials, more efficient cryo-grinding in liquid nitrogen strongly affected the results of analysis. For example, grinding the same paint material before analysis gave a value of 3.3% as compared to 2.7%. Another portion of this material was cryo-ground prior to mixing in a ball mill yielding a value of 4.3% which is more in agreement with the 4.13% value obtained by microwave digestion/atomic absorption spectrometry. These preliminary data indicate that sample homogeneity and particle size play an important role in accuracy of XRF analysis. This study will be extended to include soils and dusts to develop sample preparation procedures for improving the accuracy of analysis.

8. Development of a Rapid Screening Method for Heavy Metals in the Environment Using Slurry Sample Introduction and Electrothermal Atomization Atomic Absorption Spectrometry

M.S. Epstein, S.M. Smith (Yorktown High School, Arlington, VA), and J.J. Breen, (OPPT, USEPA)

The ideal analytical method for the assessment of environmental contamination by toxic elements should be rapid and cost-effective, while retaining enough accuracy and precision to allow conclusions to be drawn from the data. Most analytical techniques require the sample to be leached or dissolved in an acid medium or dissolved in a flux to obtain reasonably accurate results. These sample preparation requirements reduce sample throughput and thus reduce the response time for environmental remediation.

The slurry method of sample introduction for electrothermal atomic absorption spectrometry (ETAAS) provides a unique combination of minimal sample preparation, proven accuracy, low cost instrumentation, and rapid and unattended sample throughput that makes it ideal for the evaluation of large numbers of samples for toxic element contamination. The slurry method has been used successfully by a number of researchers for the determination of toxic elements in soils and sediments. Lead is one the elements most easily determined by the slurry method, since it readily extracts into the solvent phase, thus maximizing precision and accuracy. In this investigation, lead was determined in 400 samples of paint and soil from 53 parks in Arlington County, Virginia. The soil samples were taken from the parks and from roadways near the parks. The paint samples were taken from park equipment and structures that were already chipped. Samples were stored in plastic bags and taken to the laboratory where they were crushed and mixed. Two ~10 mg samples were taken from each bag and placed into plastic autosampler cups, with the subsequent addition of 1 mL of a diluent solution consisting of 5% (v/v) HNO_3 and 0.01% (v/v) Triton X-100. They were then analyzed using an ETAAS instrument with Zeeman-effect background correction at a low-sensitivity spectral line of lead to provide a working range that would cover the concentrations of lead in soil and paint considered hazardous. Analysis results were consistent both between and within samples in most cases, reflecting adequate homogeneity of most of the prepared samples. Soil lead concentrations were found to vary between 0 and 400 μg Pb/g, and paint lead concentrations varied from 0 to 8% Pb.

This survey was intended primarily as a test of the speed, accuracy, and precision of the slurry ETAAS method when applied to a real analytical problem, and as a very cursory evaluation of lead-poisoning dangers in public parks. The only major limitation of the slurry ETAAS method is the sequential nature of our current ETAAS instrumentation, which limits the range and speed of multielement analysis on selected samples. However, the methods used here are readily adaptable to currently-available multielement ETAAS instrumentation.

9. Chemometric Methods Development for High Accuracy and Precision Analysis of Advanced Materials Using Array Detector ICP-AES

M.L. Salit

Application of advanced spectroscopic technology to analytical ICP atomic emission spectrometry (ICP-AES) offers new and better ways to make spectral measurements. State-of-the-art spectroscopy is being performed with "camera-like" array detectors which yield simultaneous, time-correlated and complete spectra in the wavelength range of interest. Exploiting the character of these spectral measurements to improve the performance of the analytical method is the goal of this research program.

Typical ICP-AES method development is performed by an analyst selecting analytical wavelengths, internal standard elements and wavelengths, and measurement conditions based upon a set of heuristic guidelines within the limitations of the technique and equipment. The virtually limitless combinations afforded by array detector instruments demand a better way to select rationally among the choices.

We have developed several approaches for rational methods development for the bulk analysis of advanced materials (pure materials, high T_c superconductors, alloys) in which the analyte is at reasonably high levels. The performance of such analyses rivals those using definitive techniques such as titrimetry and gravimetry, while typically requiring less time and allowing smaller sample sizes. One approach for the selection of an internal standard element and wavelength is founded on the study of correlated time series. Through visualization of the time correlation of analyte signal(s) with potential internal standard signals, optimal selection can be achieved. This approach requires truly simultaneous, background corrected spectra, such as are only practically measured with array detector instruments. Another approach, with potential for further performance enhancement, and application to multielement analysis is based on a variance-based statistical method known as Principle Component Analysis (PCA). PCA is used here to first identify elements which co-vary, and then to create an optimal, artificial internal standard signal which is a combination of the pure element signals. One character of PCA is to reduce the number of dimensions of a dataset (elements/wavelengths) to a small number of psuedo-variables (principle components) which accommodate all of the variance of the dataset. Our proof-of-concept examination of the use of a principle component as an internal standard has been promising, yielding general improvements of 20-50% in analyte signal-to-noise. In combination with the correlation visualization approach for selection of dataset variables, this approach allows a spectroanalyst to exploit state-of-the-art instrument technology.

Continued work in this program will focus on characterizing analytical performance with these method development techniques and extension to multielement analysis. We will evaluate these approaches for robustness and general utility through their application to analytical problems.

10. Development and Characterization of a Glow Discharge Atomic Emission Instrument for Macro-scale Elemental Composition Mapping of Solid Surfaces

M.R. Winchester and M.L. Salit

Practical macro-scale composition mapping would address problems ranging from the bulk homogeneity of materials used in the fabrication of microelectronic devices to the characterization of large-scale features on semiconductor wafers. We have developed a glow discharge (GD) atomic emission system to make spatially resolved measurements across dimensions of several hundreds of cm^2.

Characterization of surface morphology and mapping of elemental composition is typically performed in microscopic domains. State-of-the-art composition mapping techniques, such as secondary ion mass spectrometric (SIMS) imaging, map at sub-micron spatial resolution. The physical dimensions over which such an analysis takes place are usually very limited, owing to the extended time necessary for the analysis and the huge amount of data produced. Although it is not a composition mapping technique, an illustrative example can be taken from scanning probe microscopy. It has been estimated that fully mapping the surface of an 8-inch diameter wafer would require 6 million years and 1 billion GB of data, assuming one 1 x 1 micrometer scan per minute and 500 kB per scan.

Our GD source consists of multiple discharges, sustained simultaneously. Each discharge radiates atomic emission characteristic of the composition of the area of the sample beneath it. Spatial separation and individual monitoring of the discharges allows for the compilation of a spatio-chemical "map." Two configurations of this novel glow discharge source have been examined using a spatial multiplexing/demultiplexing technique called Hadamard Transform Spatial Imaging (HTSI). HTSI allows simultaneous monitoring of more than half of the discharges with a single detector, permitting depth profiling along with the 2 lateral dimensions of mapping. This property, along with the simplicity of moving only 1 part (a shutter mask) in 1 dimension made HTSI an attractive approach.

Optically coupling the spatial sorting scheme — HTSI — with the spectral sorting scheme — high resolution grating spectrometry — proved to be a significant technical challenge. In fact, such tremendous losses in light throughput efficiency were required to couple these schemes, that we were unable to characterize the second, larger, source configuration with this approach. The 2 source configurations differed by both the number of individual discharges (15 arrayed in a 3 by 5 grid, and 63 arrayed in a 9 by 7 grid), and the discharge size and overall map area. The differences in configurations made the second, larger source, composed of smaller discharges with smaller aspect ratios, impossible to couple to the spectrometer.

Continued work on this compositional mapping technique will utilize an alternate spatial sorting approach — rapid translation of the source with respect to the spectrometer coupling optics, allowing near-simultaneous monitoring of individual discharges, with no multiplexing involved. The flexibility of this approach will allow random access of any spatial location of the source, allowing arbitrary sampling locations to be established as appropriate for the application requirements. A program to test this method with materials from relevant application areas is being established, and will be pursued in the coming fiscal year.

11. Laser-Enhanced Ionization Mass Spectrometry in Flames

G.C. Turk and L. Yu

The major impediment to measurement accuracy in trace and ultra-trace analysis is chemical matrix interferences. This work combines aspects of two existing approaches to ultra-trace elemental analysis, laser-enhanced ionization spectroscopy (LEI) and inductively coupled plasma mass spectrometry (ICP-MS), with the goal of improving measurement accuracy through enhanced elemental specificity. This is possible by combining the optical atomic spectroscopic selectivity of LEI with mass spectrometric selectivity. A complementary nature exists between LEI and ICP-MS which makes their combination advantageous. In LEI, a laser tuned to an atomic transition wavelength selectively ionizes atoms, usually in a flame, and the enhanced ionization is detected as an increase in the electrical conductivity of the flame. This conductimetric detection is non-selective, and interferences can occur in situations where the laser excitation results in ionization of atoms or molecules other than the intended analyte. In ICP-MS, all species with ionization potentials low enough to be thermally ionized in the 6000 K ICP are ionized without specificity, and the selectivity of the measurement is provided solely by the quadrupole mass spectrometer. Isobaric interferences often occur, and are the most serious impediment to the measurement accuracy of ICP-MS. Since ICP-MS is firmly established as the method of choice for trace and ultra-trace elemental analysis, with many industrial, environmental, and health related applications, the susceptibility of the method to isobaric interferences has many potential repercussions.

We have used laser excitation to selectively ionize atoms at atmospheric pressure in high temperature sources by LEI, and detected the resulting ions mass spectrometrically, using a differential pumping system to draw the ions into a vacuum. A commercially manufactured ICP mass spectrometer has been modified for this purpose, replacing the high temperature ICP ion source with a lower temperature air-hydrogen flame. This replacement is necessary to provide an environment which converts sample to free atoms, rather than ions, thus leaving the ionization process to LEI. Thus far sodium, calcium, iron and potassium have been detected in this manner, with LEI induced by a dual wavelength excimer pumped dye laser system. Initial investigations have centered on the study of the transport of the LEI ions from the flame to the mass spectrometer, and the effects of ion-electron recombination or flame chemistry on the process. The results appear promising, with high signal-to-noise ratios observed at trace concentrations.

12. Determination of the Transmittance Uniformity of Optical Filter Standard Reference Materials

J.C. Travis, N.K. Winchester, and M.V. Smith

The Optical Filters Program of the Inorganic Analytical Research Division of NIST produces Standard Reference Material (SRM) optical filters, solutions, and purified chemicals, certified for their transmittance, transmittance density, or specific absorptivity at a variety of wavelengths throughout the ultraviolet and visible spectral regimes, with near infrared (NIR) filter standards under development. Unlike solution standards, solid filters require individual certification of their transmittance using the Analytical High Accuracy Spectrophotometer (HAS), because neither the thickness of absorbing glass filters nor the evaporative coating thickness for metal-on-quartz filters may be adequately controlled for batch certification. Furthermore, the filters are certified over an area of one-to-two mm wide by 8-mm high, centered in the filter, as determined by the geometry and convergent beam of the HAS. Inasmuch as the beam geometry of end users may vary from that of the certifying instrument, a tolerance for transmittance homogeniety has been established for each class of optical filter standard over a 6 by 24 mm area, and individual filters have been accepted or rejected on the basis of a test using a scanning densitometer of NIST design and construction.

The maturity of scientific grade digital cameras based on charge coupled device (CCD) solid-state detector arrays has provided an opportunity to enhance the filter evaluation process. The linearity of these devices over a large dynamic range is sufficient to resolve the transmittance variations of interest, while the number of detection elements is adequate to examine multiple filters simultaneously, while still providing higher spatial resolution than the former instrument. The simultaneous acquisition of data over the area of interest of each filter minimizes the impact of temporal light source drift, and relaxes the requirements for absolute source stability.

The FY94 work represents the performance qualification of a new CCD camera-based instrument for homogeneity evaluation. The emphasis of the study is on the direct replacement of the older instrument, with intentional degradation of the camera resolution by pixel averaging. The following observations may be applied to the new CCD camera system: 1) The camera system yields sufficient results-conformity with the scanning densitometer to take over the functions of the latter. 2) The new system improves throughput by examining multiple filters in parallel. 3) Parallel examination of all areas of a filter reduces the importance of source stability, permitting the use of a more intense source with concommitant improvement in relative random uncertainty. 4) The numerical, statistical treatment of high (spatial) resolution data to determine millimeter scale homogeneity results in an uncertainty estimate for each measured transmittance deviation, a feature not present in the older instrument. 5) Visual observation and analysis of contrast-enhanced high resolution images may help improve the production quality of optical filter standard reference materials.

Future studies anticipate use of the system to identify sources of inhomogeneity and improve filter production quality, and to address the homogeneity issue for end user systems which illuminate narrower portions of the sample than the NIST instrument. For anticipated absorbance standards in the NIR, the instrument may be operated with an interference filter at an appropriate wavelength.

13. Determination of Sodium and Calcium in Blood Serum by ICP-MS

S.E. Long and J.D. Fassett

High accuracy measurements on clinical materials are provided by NIST as part of a long-standing cooperative program with the College of American Pathologists (CAP). Although in the past this program has focused on the determination of organic analytes, it has recently been expanded to cover several inorganic components such as electrolytes and trace metals. For this program, there is a need to provide analytical methods which are as efficient and streamlined as possible, and therefore two new methods for the determination of sodium and calcium in lyophilized blood serum have been developed. For certification purposes, these analytes are usually determined by gravimetry and isotope dilution thermal ionization mass spectrometry respectively. Although capable of very high accuracy, these methods are comparatively slow. In contrast, ICP-MS is capable of high sample throughput, while providing comparable accuracy. The accurate determination of sodium and calcium by quadrupole ICP-MS has not usually been considered feasible. Sodium is subject to a high instrumental background, while calcium has severe spectral overlap interferences on all of its major isotopes.

In the new procedure for sodium, a cross between isotope dilution analysis and internal standardization was employed. The reconstituted serum was diluted by a factor of fifty, and spiked with ^{26}Mg separated isotope. The isotope ratio ^{23}Na/^{26}Mg was then measured using ICP-MS configured in an analog detection mode. Because the serum also contains a small concentration of magnesium, the ratio ^{24}Mg/^{26}Mg was also measured and the ^{23}Na/^{26}Mg ratio internally corrected for the serum background ^{26}Mg contribution. This correction was of the order of 0.1%. The ratios were standardized by using a sodium primary standard (SRM 919) spiked with ^{26}Mg. The precision of measurement of the isotope ratios was of the order of 0.05-0.15%. As a relatively high concentration of sodium was determined in the analog detection mode (50 μg/mL), the instrumental sodium background was relatively small.

For the determination of calcium, an isotope dilution analysis scheme was used. As the major isotopes of calcium are severely interfered with by molecular ions derived from the instrument, the minor isotopes ^{43}Ca and ^{46}Ca, were used as the measurement pair. The reconstituted serum was spiked with ^{46}Ca and digested using a mixture of nitric and perchloric acids. The calcium was then separated from sodium and other constituents using cation exchange. The complete separation of sodium was important in order to avoid interference from a sodium dimer peak at mass 46 during the ICP-MS measurement process. Because of the relatively high concentration of calcium in blood serum, it was possible to achieve sufficiently high count rates on the minor isotopes for optimizing isotope ratio measurement precision. The precision of measurement of the isotope ratios was of the order of 0.1-0.2%. The method was validated by concurrent measurements on the same samples using thermal ionization mass spectrometry.

Both of these procedures have been used to provide high accuracy measurements of CAP serum reference materials. During the certification process for the replacement blood serum SRM 909b, it is planned to further validate the ICP-MS method for sodium by comparison with the classical gravimetric definitive method.

14. Development of a Loss-Free Dissolution Procedure for Determining Chromium in Botanical Materials

R.R. Greenberg, T.W. Vetter, and K.M. Garrity

Chromium plays an important role in biological processes. It is essential for glucose and lipid metabolism in both plants and animals, yet in certain forms chromium is toxic at levels that are only a few orders of magnitude higher than are nutritionally required. For many analytical techniques, chemical dissolution or fusion is the first step in the analytical procedure. However, losses of chromium during the dissolution process are a problem in the analysis of botanical materials. Possible loss mechanisms include: gaseous evolution during decomposition, absorption onto surfaces, precipitation, and persistence of undissolved material due to the presence of various soil and/or mineral fractions that are difficult to totally solubilize.

In previous studies, concentrations of 20 elements were measured non-destructively using instrumental neutron activation analysis (INAA) and these results were compared with results from other analytical techniques that require sample dissolution. Of the twenty elements measured, chromium showed the lowest recovery with losses ranging from 2% to 30% of the total chromium present. For several of the dissolution methods used, the chromium was present in an insoluble mineral fraction. For this reason, experiments were performed to determine optimum conditions for the complete dissolution of botanical materials.

Four different botanical materials were analyzed, SRM 1515 Apple Leaves, SRM 1570 Spinach Leaves, SRM 1547 Peach Leaves, and SRM 1573 Tomato Leaves. The procedure consisted of irradiating aliquots of each, INAA of these for chromium prior to dissolution, and then subjecting these same aliquots to specific dissolution conditions. Two methods of dissolution were used, an open vessel with conventional heating and a closed vessel for the microwave oven dissolution. With the appropriate conditions, the use of a microwave system allows for complete dissolution in far less time as compared with that for an open-vessel dissolution; because the microwave dissolution vessels are closed systems, the probability of evaporative losses are minimized. For each of these methods, the type and amount of each acid, the temperature (and pressure for the microwave dissolution method) experienced by the sample, and the duration of exposure to a given set of conditions were optimized. For most samples, the dissolved material was filtered and then the filter and liquid were analyzed for chromium by radiochemical NAA. The extent to which total dissolution was achieved was determined by comparison with INAA results for the undissolved material.

Further data acquisition and analyses are in progress. However, preliminary results for the spinach leaves show that any chromium remaining on the filters is below detection limits. Future work will include optimizing of this procedure and analysis of additional botanical materials using the same conditions and the development of a procedure for additional matrices.

15. Preliminary Evaluations of a New Neutron Focusing Lens for Materials Characterization

D.F.R. Mildner, R.G. Downing, R.L. Paul, R.M. Lindstrom, C.J. Zeissler, H. Chen(University of Missouri), V.A. Sharov (X-Ray Optical Systems, Inc.), and Q.F. Xiao (X-Ray Optical Systems, Inc.)

Prompt gamma activation analysis (PGAA) is a non-destructive technique used to simultaneously identify multiple elements and determine their concentration in a variety of samples. At present PGAA is primarily a tool for bulk analysis. This is due to insufficient neutron flux, even at research reactors, despite improvements made through the use of neutron guides and cold neutron sources. To enhance the detection limit of PGAA on decreasing sample sizes and to provide lateral spatial resolution for two dimensional compositional mapping, we have developed a polycapillary neutron lens, custom designed for the cold neutron PGAA facility at NIST. The lens, made with 1763 lead-silica glass polycapillary fibers, accepts a polychromatic cold neutron beam (wavelengths higher than 0.4 nm) from a neutron guide, 50 mm x 45 mm in cross section, and delivers a focused beam of 0.5 mm in diameter (full width at half maximum) at 52 mm from the exit of the capillaries. The average neutron current density at the focus is 80 times higher than that of the direct incident beam.

Preliminary PGAA measurements using the lens have been performed on test samples of a 2% gadolinium glass particle (0.23 mm x 0.385 mm) and a cadmium metal particle (0.50 mm x 0.45 mm). The prompt gamma count rates for the Gd 182 keV and the Cd 558 keV peaks were monitored. The gain in the prompt gamma signals is defined as the ratio of the count rate with the lens to that without the lens, representing the enhancement in the total absorption rate by using the lens. The gains obtained are 58.3 ± 10 and 66.7 ± 0.8 for the Gd and Cd samples, respectively.

Additional measurements have also been performed to demonstrate the spatial resolution in one dimension using a known boron distribution. In these experiments a 1 mm ^{6}LiF aperture is placed at the focal plane to define the focused beam. Samples are glass polycapillary fibers, similar to those used in the construction of the focusing lens except differing in composition. A row of lead-silica and borosilicate (8 wt.% boron) fibers (5 each, 0.4 mm in diameter) is arranged alternately (B-Pb-B-Pb...), side by side, behind the aperture. The prompt gamma count rate for the boron peak at 478 keV is monitored as the row of samples is scanned in the horizontal direction along the focal plane. The count rate is maximized when a borosilicate fiber centers in the focus and is minimized when a lead-silica fiber centers, forming an oscillating prompt gamma response pattern. At this submillimeter range, the peaks are partially resolved: (peak – valley)/(peak – background) ~ 38% (100% represents complete resolution). The same experiment has also been performed on a row of fibers of the same composition and arrangement as above (3 each), but of 1 mm diameter, for which a 97% resolution is obtained.

We have successfully performed preliminary evaluations of the new lens and obtained a signal gain of about 60 on two test samples, as well as achieving a spatial resolution in the submillimeter range. We are continuing efforts to reduce the neutron and gamma background and to improve the neutron transmission efficiency of the lens.

16. International Intercomparison for Trace Elements in Silicon Semiconductor Wafers by Neutron Activation Analysis

D.A. Becker, R.M. Lindstrom, and T.Z. Hossain (Cornell University)

Members of ASTM Task Group E10.05.12 (Nuclear Methods of Chemical Analysis) and a number of other scientists expressed interest in an interlaboratory comparison of the analysis of high purity silicon and silica. Despite the great economic importance and the large number of analyses by the silicon device industry, there have been almost no interlaboratory evaluations of the quality of these analyses. The only recent comparison prior to the start of this effort involved four samples analyzed sequentially in four laboratories (J. Radio-anal. Nucl. Chem. **122** (1988) 261). The results agreed within a factor of two for As, Cu, and W, and worse for Au. A workshop organized by the International Atomic Energy Agency (IAEA TEC DOC-512) at NBS in 1987 called attention to the lack of standardization in this field, and suggested that systematic interlaboratory comparisons and compositional reference materials would be of value in assessing the ability of analytical laboratories to obtain demonstrably accurate data.

In addressing this problem, the Task Group arranged to distribute four samples to each of 19 participants, as follows: (1) a silicon wafer of “moderate purity” - 10 cm diameter x 525 μm thick; (2) a silicon wafer of “high purity” - similar size; (3) a 50 mg chip of high purity silicon; and (4) a 0.5 gram sample of high purity silicon dioxide powder. The wafers were donated by Eastman Kodak Co., the other samples by another party. Participants were requested to determine the trace element composition of each of the samples according to their best standard procedures and to report the results. In order to intercompare the data, details of the methods employed were requested as well. Reflecting the makeup of the Task Group, most of the participants used neutron activation analysis (NAA) although other analytical techniques were also welcome.

Nine sets of results were returned, from six different countries: Canada, Finland, Germany, India, The Netherlands (2), and the U.S. (3). These represented government laboratories (3), universities (2), semiconductor industry laboratories (2), and private analytical laboratories (2). Results will be presented at the International Workshop on Semiconductor Characterization: Present Status and Future Needs (NIST, Jan. 30-Feb.2, 1995). Evaluation of the data shows that a total of 15 elements (Au, Na, As, Br, Ag, Co, Cr, Sb, Zn, Mn, Cu, Fe, K, O, and P) were detected on the surface and/or in the bulk wafer. A variety of activation analysis techniques were used including both instrumental and radiochemical NAA, etching the wafers after irradiation and counting both etch solution and remaining wafer to determine both surface impurity concentrations as well as bulk impurities, and determination of O and P by charged particle (a) activation analysis. As expected, more elements were found in the surface impurities (up to 14 elements) than in the bulk material after etching(up to 8 elements). Finally, the range of values obtained for one element (Au, with no prior cleaning of the wafer) was over 10,000 (0.5 ppb down to 0.03 ppt (wt. %)). This data strongly supports the need for improved methods of standardization and accuracy evaluation.

17. Toxic and Essential Trace Elements in Marine Mammal Liver Tissues

R. Demiralp and E.A. Mackey

The National Oceanic and Atmospheric Administration (NOAA) supports two marine mammal specimen banks within NIST's National Biomonitoring Specimen Bank, the Alaska Marine Mammal Tissue Archival Project (AMMTAP) and the National Marine Mammal Tissue Bank (NMMTB). Tissues comprising the NMMTB are taken from stranded animals that cannot be either rehabilitated or returned to the ocean, and tissues comprising the AMMTAP are taken from animals captured by Native Alaskans during subsistence hunts. The purpose of these tissue banks is to determine long-term trends in the marine environment, determine whether anthropogenic activities impact the marine mammal population, and to have the ability to perform retrospective analyses in the event new contaminants are identified in the future. In collaboration with the Organic Analytical Research Division, the Inorganic Analytical Research Division performs analyses on a subset of the banked tissues to provide quality assurance for other NOAA laboratories that are responsible for the analysis of these and other marine mammal tissues and to contribute to the trace element and contaminants database for marine mammals.

Instrumental neutron activation analysis (INAA) is used for determination of trace element constituents because a large number of elements can be determined from a single aliquot of tissue. During the past year, liver tissues from 11 mammals were analyzed for 35 elements and tissues from 24 mammals were analyzed for mercury. These analyses provided data for three species of banked samples that were not previously analyzed, the white-sided dolphin, bearded seal and spotted seal. Results from these analyses were compatible with results of previous analyses of other marine mammals; most values were within the ranges previously observed.

Of special concern are the levels of toxic elements in liver tissues of the Alaska marine mammals because these tissues comprise part of the diet of the Native Alaskans. Ringed seal liver tissues were included in this most recent analysis not only to increase the database for ringed seals but also to determine whether previously observed levels of as much as 2 mg/kg of arsenic were pervasive in the ringed seal population from Nome. Although the levels of arsenic are not high enough to pose a serious health risk, levels found in two of the ringed seal livers measured previously were approximately one order of magnitude higher than the highest value found in beluga livers. Results from analyses on an additional four ringed seal livers taken from animals in the same region yielded values ranging from 0.2 to 0.9 mg/kg. Values for cadmium and mercury in these tissues ranged from 0.1 to 4 mg/kg and are also not considered to be a health risk.

Current plans for FY95 are to analyze an additional 12 livers from both the AMMTAP and the NMMTB. Analyses of the remaining harbor porpoise tissues will complete the data set for banked tissues of this species. Analyses of liver tissues from walrus will provide information on trace element levels in a species that represents the top of the Arctic food chain and one that has not yet been analyzed for the AMMTAP. Analyses of two California sea lions will provide results for yet another species for which there are banked tissues and provide information on levels in animals from another geographic region. Additional analyses may also be included in support of the quality assurance aspect of the NOAA programs.

18. New Developments in Hydrogen Determination by Cold Neutron Prompt Gamma Activation Analysis

R.L. Paul and R.M. Lindstrom

There has long been a need for reliable hydrogen determination at low concentrations. We have found cold neutron prompt gamma-ray activation analysis (CNPGAA) to be suitable for measurement of H in a wide variety of materials. The method is nondestructive, measures the entire sample, and the results are independent of the chemical form of H present. The NIST system, constructed as part of the Cold Neutron Research Facility (CNRF), uses a pure beam of long-wavelength neutrons to induce neutron capture by hydrogen, resulting in emission of a characteristic gamma-ray at 2223.23 keV. Because the H background is low, the detection limit in some materials is below 10 μg.

Recent developments in the CNPGAA instrument have greatly improved its measurement capabilities. The installation of a helium-purgeable, vacuum-tight sample chamber has reduced the hydrogen background by a factor of two. The addition of a bismuth germanate (BGO) Compton shielding detector has reduced the spectrum baseline by up to a factor of six, yielding better signal-to-noise ratios and improved detection limits for H and other elements.

A significant effort has been made to develop CNPGAA as a reliable technique for the analysis of trace hydrogen in metals. We previously reported measurement of up to 750 ± 50 mg H/ kg Ti (several times the maximum permitted H concentration) in a titanium alloy compressor blade from a failed jet engine. After the addition of Compton suppression to the instrument, H levels as low as 50 mg H/ kg Ti were measured in two new compressor blades. CNPGAA has also been used to measure concentrations of 128 ± 33, 181 ± 45, 14400 ± 800, and 19900 ± 1000 mg H/ kg Ti in four titanium alloy hydrogen standards prepared for neutron tomography experiments. Most recently we have used CNPGAA in conjunction with small angle neutron scattering to study the effects of hydrogen impurity and pore size in samples of nanocrystalline Fe, Cu, and Pd.

CNPGAA has found application in the analysis of hydrogen in a variety of other materials, including specimens of pure and substituted fullerenes, and crystals of hydrothermal quartz and semiconductor grade germanium. The method has also been used to study the uptake of hydrogen by proton conductors. Concentrations of 2-3 mole percent hydrogen were measured in Yb-doped samples of $SrCeO_3$, in agreement with H measurements using a thermobalance. Further measurements of H in proton conductors are planned.

Future improvements in the CNPGAA instrument will result in improved detection limits for hydrogen, smaller measurement uncertainties, and shorter analysis times. These include the replacement of the deuterium ice cold source with a liquid hydrogen moderator, improved neutron and gamma-ray shielding, and continued fine tuning of the Compton shield electronics. The addition of a neutron focusing capillary lens will yield better detection limits for small (< 1mm) samples and higher lateral resolution for samples with compositional variations. The development of reliable hydrogen standards and blanks for titanium and zirconium will result in improved hydrogen determinations for these metals. Plans are also underway to develop a reliable method for determining hydrogen in partially deuterated polymers by prompt gamma activation analysis. However, since the major inaccuracy in determination of hydrogen at higher concentrations (>1%) is the effect of neutron scattering on reaction rates, further studies of this process are needed in order to increase the reliability of these measurements.

19. Characterization of Diamond Films by Neutron Depth Profiling for Semiconductor Applications

G.P. Lamaze, R.G. Downing, and K. Coakley (CAML)

Because of their physical properties, much interest has been shown in diamond and diamond-like materials to construct high-current semiconductor devices. Among the most important of these physical properties are the highest known thermal conductivity (20 W/cm/K), wide energy gap (5.5 eV) and high breakdown fields (10^7 V/cm). Natural type II diamond crystals are known to be semiconductors with boron as the dominant acceptor with an activation energy of approximately 0.3 eV. During the synthesis of thin diamond films, dopants such as boron or nitrogen can be added and the amount of the dopant controlled by varying gas mixtures and other parameters. The first boron-doped synthetic diamond field-effect transistors have been recently announced. The concentration and the distribution of boron and nitrogen in thin films can be determined by neutron depth profiling (NDP). Depth profiles of about one micrometer are measured with little interference. The technique is non-destructive which allows sample modification and remeasure as well as comparison with other measurement techniques. During the past year we have analyzed synthetic diamond samples from the Pennsylvania State University (PSU) and the University of Konstanz (Germany).

With PSU we measured the distribution of boron in diamond films before and after annealing to 1100 °C and established that the boron was stable implying that the boron was substitutionally located in the diamond lattice. Measurements were also made on samples where nitrogen doping was attempted on homoepitaxially grown diamond films. We did not detect the presence of nitrogen and reported an upper limit of 250 atom ppm of nitrogen in the diamond lattice. With the University of Konstanz, we made high resolution measurements of boron doped multilayers in diamond-like films. Using the results from this sample, the Computing and Applied Mathematics Laboratory has developed a computer code that calculates the effects of straggling as a function of depth and then extracts the original boron distribution of the sample. The distribution of nitrogen in a diamond-like multilayer film from Konstanz was also measured. This sample differed from the PSU sample in that it was epitaxially grown on a silicon substrate and the nitrogen was added by ion bombardment.

During the coming year, the cold neutron source at the reactor is being upgraded and the cold neutron depth profiling facility will move to the end of a curved neutron guide. The curved guide should dramatically lower the gamma-ray background and coupled with the higher fluence rate of the new cold source, we expect about two orders of magnitude improvement in our nitrogen measurement capability. We also plan to make use of a neutron lens that focuses the neutron beam to a 1 mm diameter spot. This is especially important for homoepitaxially grown diamond samples which are typically only 2 mm x 2 mm. For samples of this size, better than an order of magnitude improvement in counting statistics is expected over the non-focused beam. Data analysis will lead to better depth distribution information and will provide more automated data analysis techniques which will improve turn-around time for our customers and collaborators.

20. Development and Application of Negative Thermal Ionization Mass Spectrometry

R.D. Vocke, E. Widom, P. Morales, and J.D. Fassett

The first practice of isotope ratio negative thermal ionization (NTI) mass spectrometry occured at the National Bureau of Standards (NBS) in the 1960s, when procedures were developed for the elements chlorine and bromine. The NBS thermal ionization instruments were designed to accommodate the measurement of ions of either polarity. Recently NTI has seen a renaissance with the development of procedures for a number of electronegative elemental and molecular species that cannot be done readily using positive thermal ionization. These elements include Se, Tc, Os, Re, Ir, Pt, and Pd. In the past year, we have modified an NBS thermal ionization mass spectrometer in order to optimize its efficiency in the negative ion mode of operation and have applied this instrument to studies of the osmium/rhenium geochemical isotopic system.

One of the problems specific to NTI is the adverse effect of electrons on the ion optics, especially catastrophic electrical breakdown in the source. The operational response to this problem has been to do NTI at lower accelerating potentials; however, no allowances were made for observed differences in the ion focussing parameters between positive and negative ionization. We have now modified the standard NBS thermal ionization source to make it more rugged for negative ions. The ion acceleration is larger initially and more constant through the lens which makes the lens more robust against arcing. And, transmission efficiency is higher at the lower accelerating potential for negative ions. The new design brings single filament ion trajectories to a focus just prior to the alpha slit. It is a more open design, so that permanent magnets can be incorporated to suppress electron movement in the source. We have measured the magnetic field in the immediate vicinity of these magnets using a precisely positioned Hall-probe assembly to model the effect of magnet positioning and to optimize their placement.

Two other modifications were made to generally improve the flexibility of this thermal ionization instrument. First, a high quality variable leak was incorporated in the source of the mass spectrometer. This leak will allow controlled and reproducible introduction of oxygen (or other gases) into the source which is correlated with efficient negative oxide ion production. In addition, a Faraday cup/electron multiplier detection system has been designed and installed. These detectors will allow an increased dynamic range for either positive or negative ionization studies.

The barium hydroxide loading method for negative thermal ionization has been applied to Re, and the high sensitivities achievable by the NTI method demonstrated: 1×10^{-11} amperes from 100 pg of Re. This remarkable efficiency for negative ionization of rhenium was accompanied by the observation of a significant blank, equivalent to several picograms. We have reduced this blank by a factor of 10-50 by disassembling the source chamber and thoroughly cleaning all exposed surfaces. Obviously, at high sensitivities, blank and memory are as critical an issue for negative ionization as they are for positive ionization. In FY95, we plan to continue validation experiments. This instrument will expand the capability for high precision isotope ratio measurement at trace and particularly ultratrace levels for both positive and negative ions.

21. Investigation of Suitable Solvents for Selected Element Determinations by ICP-MS Isotope Dilution

E.S. Beary and P.J. Paulsen

The Inductively Coupled Plasma Mass Spectrometer (ICP-MS) is a powerful analytical instrument that combines an efficient, non-specific plasma source with ion extraction directly into the vacuum of the mass spectrometer. The most accurate method for ICP-MS quantification is isotope dilution (ID) which relies on rapid, sequential measurement of samples and controls to minimize and correct for short and long term drift. Rapid measurement requires that the memory from a previous sample be reduced to no more than 0.1% within two minutes. Crosstalk among samples is one of the most persistent and troubling problems with sequential solution sampling, especially when quantified by ID. Certain elements have notoriously long retention times under routine instrumental conditions due to adsorption/absorption to plastic, glass or other hardware, in addition to element volatility in the spray chamber. We have identified chemical methods for reducing memory for several problematic elements, including B, Hg, Ag, and Mo. Specific solvents for each element are used in the measurement sequence to "washout" the analyte between samples.

Boron's instrumental memory is caused primarily by its volatility. During a single five minute run, the absolute signal intensity for boron in a dilute HNO_3 solution can rise up to 50%. This increased signal is due to volatile residual B from a previous sample(s). A dilute NH_4OH solvent reduces residual boron to 1% after a two minute wash, a marginal improvement over dilute HNO_3 and HCl solvents which leave 5% boron. We found that NH_4OH/mannitol solvent reduced boron to <0.1% in only 40 seconds. Similarly, long term and slowly changing memory plagues Hg determinations. The addition of dichromate or permanganate to a dilute HCl solvent reduces the Hg memory to about 0.5% after two minutes. However, we found that both HBr and HI drop residual Hg to <0.1% after only a 30 second wash.

Molybdenum and silver pose a different problem. Both elements can precipitate or form a colloidal suspension in the prepared sample solution prior to and/or during instrumental analysis, degrading the precision of the ratio measurement. Dilute NH_4OH prevents the loss of Mo, maintains a constant signal intensity during instrumental analysis, and provides the expected ratio measurement precision. We found that when Ag and Hg are both present in a sample solution, the Hg is preferentially reduced/adsorbed. Therefore, a dilute NH_4OH solution containing Hg is used as the solvent for the Ag determinations.

These procedures improved our ability to make both accurate and precise ratio measurements and to determine these elements in environmental materials. In all cases the solvents of choice were prepared in bulk supply, and used both as wash solutions and sample solvents. In this manner, the solvent background, which is automatically subtracted, is as stable as possible. These procedures are applicable to methods of sample introduction, such as online liquid chromatography or automation using flow injection analysis.

C. Outputs and Interactions (Inorganic Analytical Research Division)

1. Publications

Anderson, D.L., Downing, R.G., and Iyengar, G.V., "Trace Elements in Food Reference Materials: Compositional and Analytical Perspectives," Fres. J. Anal. Chem. (in press).

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Downing, R.G., "Neutron Depth Profiling Analysis," Chalk River Laboratories, Atomic Energy of Canada-Limited, Chalk River, Ontario, Canada, August 17, 1994.

Downing, R.G., "Applications of Neutron Depth Profiling and Prompt Gamma Activation Analysis," Frank Laboratory, Joint Institute for Nuclear Research, Dubna, Russia, September 27, 1994.

Epstein, M.S., "Application of a Novel Slurry AAS Protocol for Rapid Environmental Assessments," 208th American Chemical Society National Meeting, Washington, DC, August 23, 1994.

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Kelly, W.R., "Determination of Trace Elements in Solids by Isotope Dilution Thermal Ionization Mass Spectrometry," 20th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Detroit, MI, October 21, 1993. Invited

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Lindstrom, R.M., "Prompt-Gamma Activation Analysis and Applications in Industry, the Environment, and Medicine," International Workshop on Neutron Research and Applications, Budapest, Hungary, March 24, 1994.

Lindstrom, R.M., "Recent Scientific and Engineering Activities at the NIST Reactor," Interfaculty Reactor Institute Colloquium, Technical University, Delft, The Netherlands, May 16, 1994.

Lindstrom, R.M., "Elemental Analysis with Neutron-Capture Prompt Gamma Rays," Analytical Department, DSM Research, Geleen, The Netherlands, September 7, 1994.

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Paulsen, P.J. and Beary, E.S., "Determination of Trace Elements in Solids by ICP-MS Isotope Dilution: Certification of NIST SRMs," FACSS, Detroit, MI, October 6, 1993.

Paulsen, P.J. and Beary, E.S., "High Accuracy Analysis of Trace Elements in NIST SRMs by ICP-MS Isotope Dilution," Alfred O. Nier Symposium on Inorganic Mass Spectrometry, Durango, CO, May 11, 1994.

Pella, P.A., "Development of Thin Film Standard Reference Materials for XRF Calibration," Australian X-Ray Analytical Association-Solutions to Everyday Problems, University of Queensland, Queensland, Australia, October 1, 1993.

Pella, P.A., "Standards for XRF," a Tutorial Workshop, 43rd Annual Denver Conference on Applications of X-Ray Analysis, Steamboat Springs, CO, August 2, 1994.

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Pratt, K.W., "Quantitation and Minimization of Systematic Errors in the Coulometric Assay of $K_2Cr_2O_7$," 208th American Chemical Society National Meeting, Washington, DC, August 27, 1993.

Salit, M.L., "NIST CAALS: Behavior for Instrument Controllability," 1994 Pittsburgh Conference Chicago, IL, March 2, 1994.

Salit, M.L. and Winchester, M.R., "Macro-scale Compositional Mapping of Solid Surfaces with Plasma Atomic Emission Spectroscopy," 1994 Winter Conference on Plasma Spectrochemistry, San Diego, CA, January 12, 1994.

Salit, M.L., Watters, R.L., Jr., and Wood, L.J., "Analytical Experiences with Array Detector ICP-OES," 40th Canadian Spectroscopy Conference, Dalhousie University, Halifax, Nova Scotia, Canada, August 8-10, 1994. Invited

Saraswati, R. and Watters, R.L., Jr., "Determination of Arsenic and Selenium in Spinach and Tomato Leaves Reference Materials using Flow Injection and Atomic Absorption Spectrometry," 1994 Winter Conference on Flow Injection Analysis, San Diego, CA, January 5-7, 1994.

Tomaszkiewicz, I., O'Hare, P.A.G., and Beck II, C.M., "Thermochemistry of Pentatungsten Trisilicide W_5Si_3: The Vital Role of Analytical Chemistry," 49th Annual Calorimetry Conference, Santa Fe, NM, July 31 - August 4, 1994.

Turk, G.C., "The Fundamental Limit of Detection for Laser-Enhanced Ionization Spectrometry," FACSS-93, Chicago, IL, October 12, 1993. Invited.

Turk, G.C., Yu, L., Koirtyohann, S.R., and Salit, M.L., "Selective Laser-Induced Ionization in Inductively Coupled Plasma Spectrometry," Winter Conference on Plasma Spectrochemistry, San Diego, CA, January 11, 1994.

Turk, G.C., Yu, L., and Koirtyohann, S.R., "Resonance Ionization Spectroscopy in Atmospheric Plasmas with Mass Spectrometric Detection for Trace Analysis," 7th International Symposium on Resonance Ionization Spectroscopy and Its Applications, Bernkastel-Kues, Germany, July 4, 1994.

Vetter, T.W., Pratt, K.W., Turk, G.C., Beck II, C.M., and Butler, T.A., "Using Instrumental Techniques to Increase the Accuracy of Classical Analyses in the Gravimetric Determination of Sulfate," American Chemical Society National Meeting, San Diego, CA, March 13, 1994.

Vetter, T.W., "Integration of Instrumental Techniques with Classical Gravimetry to Increase the Accuracy and Precision of Analysis," 208th American Chemical Society National Meeting, Washington, DC, August 21, 1994.

Vocke, Jr., R.D., "Mathematical Models for the Petrogenesis of the Harzburger Gabbro, Germany," University of Maryland Geology Colloquium, College Park, MD, October 8, 1993. Invited

Vocke, R.D., "Li Isotopic Standards and Materials," Consultants Meeting on Stable Isotope Standards and Intercalibration, International Atomic Energy Agency, Vienna, Austria, December 1, 1993.

Vocke, R.D., Morales, P., and Kelley, R.W., 1993, "Examination of Sulfur Isotopic Standards using a Solid Source Mass Spectrometer and AsS Ions," Consultants Meeting on Stable Isotope Standards and Intercalibration, International Atomic Energy Agency, Vienna, Austria, December 1, 1993.

Vocke, R.D., "High Precision Li and B Isotopic Measurements of Natural Aqueous Samples: Approaches and Pitfalls," Consultants Meeting on Isotope Techniques in Groundwater Pollution Studies, International Atomic Energy Agency, Vienna, Austria, December 7, 1993.

Vocke, Jr., R.D., "Paleontology: Fossils and Age Dating," Adventures in Science, National Institute Standards and Technology, Gaithersburg, MD, March 5, 1994.

Vocke, Jr., R.D., "Lead and the Environment," Science Day Talk in the Red Auditorium at NIST, April 21, 1994.

Vocke, Jr., R.D., "Lead in the Environment," Analytical/Nuclear/Environmental Chemistry Colloquium, University of Maryland, College Park, MD, April 22, 1994. Invited

Vocke, Jr., R.D, Murphy, K.E., and Fassett, J.D., "The Accurate Analysis of Pb in Paint: From PPM to Weight %," American Chemical Society Annual Meeting, Washington, DC, August 21, 1994.

Winchester, M.R., Travis, J.C., Rao, A., Salit, M.L., and Marcus, R.K., "Determination of Electron Number Density in a Glow Discharge Source Using Fourier Transform Atomic Emission Spectroscopy," 20th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Detroit, MI, October 20, 1993. Invited

Winchester, M.R. and Salit, M.L., "Development of a System for Glow Discharge Atomic Emission Imaging of Solid Surfaces," 1994 Winter Conference on Plasma Spectrochemistry, San Diego, CA, January 13, 1994.

Winchester, M.R., Harville, T.R., Lazik, C., and Marcus, R.K., "Noise-amplitude Spectral Characteristics of a Radio Frequency Powered Glow Discharge Atomic Emission (RF-GD-AES) System," 1994 Winter Conference on Plasma Spectrochemistry, San Diego, CA, January 13, 1994.

3. Cooperative Research and Development Agreements (CRADAs) and Consortia

Analytical Quality Assurance in Determinations and Interpretation Related to Biological and Analytical Standardization, R.G. Downing
Biomineral Sciences, Inc. (CRADA)

Analysis of Semiconductor Materials by Neutron Beam Techniques, R.G. Downing
Intel Corporation (CRADA)

Biomedical Applications of Analytical Spectroscopy, J.D. Fassett
Eastern Analytical, Inc. (CRADA)

Effects of Radiation on the Performance of Charge Injection Devices, R.G. Downing
CID Technologies, Inc. (CRADA)

Glass Capillary Arrays for Neutron Transmission and Focusing, R.G. Downing
Schott Fiber Optics (CRADA)

Investigation of Neutron Focusing Using Capillary Optics, R.G. Downing
X-Ray Optical Systems, Inc. (CRADA)

Measurement of Noble Metals in Catalytic Converters, J.D. Fassett
Battelle Memorial Institute/Pacific Northwest Laboratories (CRADA)

Surface Properties of Refractory Transition Metal Carbides, R.G. Downing
Linfield College (CRADA)

4. Patent Awards and Applications

Salit, M.L., "Method of Correcting Spectral Data for Background," Patent No. 5,291,426 (issued March 1, 1994).

5. SRM Activities

273b	tungsten carbide
915a	calcium carbonate
924a	lithium carbonate
930e	glass filters-visible
1548a	total diet
1570	spinach leaves
1616a	sulfur in kerosene
1617a	sulfur in kerosene
1623c	sulfur in fuel oil
1624c	sulfur in diesel fuel #2
1632b	trace elements in coal
1634c	trace elements in fuel oil
1635	trace elements in coal
1640	natural water
1643d	trace elements in water
1646	estuarine sediment
1646a	estuarine sediment
1818a	chlorine in lubricating oil (Levels I-V)
1974a	mussel
2030a	glass filters
2031	metal-on-quartz filters UV-visible
2034	holmium oxide
2137	boron implant in silicon
2556	pellet auto catalyst
2557	monolith auto catalyst
2582	powdered lead paint
2583	household dust
2718	petroleum coke
2724a	diesel fuel #2
2775	sulfur in foundry coke
2776	sulfur in furnace coke
2781	domestic sludge
3101a	spectrometric solution, aluminum
3103a	spectrometric solution, arsenic
3106	spectrometric solution, bismuth
3107	spectrometric solution, boron
3109a	spectrometric solution, calcium
3113	spectrometric solution, cobalt
3114	spectrometric solution, copper
3115a	spectrometric solution, dysprosium
3116a	spectrometric solution, erbium
3117a	spectrometric solution, europium
3118a	spectrometric solution, gadolinium
3119a	spectrometric solution, gallium
3120	spectrometric solution, germanium
3122	spectrometric solution, hafnium
3123a	spectrometric solution, holmium
3124a	spectrometric solution, indium
3128	spectrometric solution, lead
3129a	spectrometric solution, lithium
3130a	spectrometric solution, lutetium
3131a	spectrometric solution, magnesium
3132	spectrometric solution, manganese
3133	spectrometric solution, mercury
3135a	spectrometric solution, neodymium
3136	spectrometric solution, nickel
3137	spectrometric solution, niobium
3138	spectrometric solution, palladium
3139a	spectrometric solution, posphorus
3140	spectrometric solution, platinum
3141a	spectrometric solution, potassium
3142a	spectrometric solution, praseodymium
3144	spectrometric solution, rhodium
3145a	spectrometric solution, rubidium
3147a	spectrometric solution, samarium
3148a	spectrometric solution, scandium
3149	spectrometric solution, selenium
3150	spectrometric solution, silicon
3151	spectrometric solution, silver
3152a	spectrometric solution, sodium
3153a	spectrometric solution, strontium
3156	spectrometric solution, tellurium
3157a	spectrometric solution, terbium

3159a	spectrometric solution, thorium
3160a	spectrometric solution, thulium
3161	spectrometric solution, tin
3163	spectrometric solution, tungsten
3166a	spectrometric solution, ytterbium
3169	spectrometric solution, zirconium
3171	spectrometric solution, multi-element
3172a	spectrometric solution, multi-element
3182	anion solution, chloride
3183a	anion solution, fluoride
3184	anion solution, bromide
3185	anion solution, nitrate
3186	anion solution, phosphate
3191	electrolytic conductivity
3192	electrolytic conductivity
3193	electrolytic conductivity
3194	electrolytic conductivity

Analytical services have been provided for the following:

Lawrence Livermore National Laboratory
McClellan Air Force Base
Northwestern University
Organic Analytical Research Division (NIST)
Reactor Radiation Division (NIST)
U.S. Naval Research Laboratory
West Chester University

6. SRD Activities

None

7. Calibrations

Special tests (transmittance filter standards) have been provided for the following:

Abbott Chemical (PR)
Abbott Laboratories (NC)
Abbott Health Products, Inc. (PR)
Abbott Laboratories (TX)
Abbott Laboratories (IL)
Allied Signal
Analytical Instrumentation
Arkansas Eastman Co.
Bacharach, Inc.

Barr Associates
Bausch & Lomb
Bio-Tech Instruments, Inc.
Boehringer Mannheim
Cal Check
Cangene Corporation (Canada)
Centocor
Central Pharmaceuticals, Inc.
Chiron
Ciba-Geigy
CMCPR
Colusa International Corporation
Corion Corporation
Corning, Inc.
Coulter Corporation
Coulter Diagnostics
Cyro Industries
D.D. Williamson Ltd.
Development Corp. (OH)
DuPont Diagnostics, Inc.
E.I. DuPont de Nemours & Co. (NC)
E.I. DuPont de Nemours & Co. (PA)
E.I. DuPont (VA)
E.I. DuPont de Nemours & Co. (TN)
E.I. DuPont de Nemours & Co. (NY)
Eastman Kodak Co.
Eli Lilly & Co.
Entergy Operations, Inc.
Ethicon, Inc. (IL)
Ethicon, Inc. (NJ)
Extractos Vegetales (Spain)
Florida Power Corporation
Ford Motor Co.
Fujisawa USA, Inc.
GBC Scientific (Australia)
GTE Control Devices
GTE California
Hach Co.
Henkel Corporation
Hewlett Packard (NY)
Hewlett Packard (DE)
Hitachi Instruments, Inc.
Honeywell, Inc.
Jasco Inc.
Juliette Metrology Lab.
Kodak Brasileria Co. Ind. Ltda. (Brazil)
Marion & Co.
Martec
Merck & Co., Inc.
Midwest Research Institute
Miles, Inc.
Milliken Chemical
Monsanto Co.
MPA NRW (Germany)
National Standards of Puerto Rico
Nichols Institute
NSPR
Nu-Tech
Organon Teknika
Ortho McNeil
Pharmaceutical Corporation
Ortho Diagnostic System Inc.
Ortho Biotech
Ortho Pharmaceuticals, Inc.
Parke-Davis
Peninsula Regional Medical Center
Pennex Pharmaceuticals, Inc.
Perkin-Elmer Corporation (CT)
Perkin-Elmer Corporation (PR)
Perkin-Elmer Corporation (OH)
Pfizer, Inc.
Polaroid Corporation
Roche Products, Inc.
Santa Barbara Research Center
Sethness Products Co.
Sherwood Medical
Shimadzu Scientific
Instruments, Inc.
Shipley Co.
Sigma Chemical Co.
Sterling Winthrop (Panama)
Sterling Chemicals, Inc. (TX)
Sterling Winthrop, Inc. (PA)
Stolle Research & Syntex
Syva
Tegimenta AG (Switzerland)
Union Carbide
UOP (IL)
UOP (LA)
USCI Division

Varian
Washington Department of Agriculture
Witco Corporation
Xoma Corporation
Zeneca

8. Committee Assignments

C.M. Beck II

ASTM, E001 Chemical Analysis of Metal, Ores and Related Materials
ASTM, E01.01 Iron, Steel and Ferroalloys
ASTM, SC.02 Ores, Concentrates, and Related Materials

D.A. Becker

ANS, SC.01 Trace Element Analysis Committee
ANS, SC.16 Isotopes and Radiation
ANS, WG.01 Activation Analysis
ANS, C004 Biology and Medicine
ANS, C006 Standards Steering Committee
ASTM, E010 Nuclear Technology and Applications
ASTM, SC.05 Nuclear Radiation Metrology
ASTM, WG.08 Nuclear Environmental Metrology
ASTM, WG.10 Neutron Metrology
ASTM, WG.12 Nuclear Methods of Chemical Analysis, Chairman

J.R. DeVoe

Chairman, EPA Special Interagency Task Subgroup on Method Development and Standards for Lead Analysis
ASTM, E06.23 Lead Paint Abatement

R.G. Downing

ASTM, F001 Electronics
ASTM, WG.11 Alpha Particle Induced Soft Errors
ASTM, E010 Nuclear Technology and Applications
ASTM, SC.05 Nuclear Radiation Metrology
ASTM, WG.12 Nuclear Methods of Chemical Analysis
IUPAC, V.7 Commission on Radiochemistry and Nuclear Techniques
Sigma Xi, The Scientific Research Society, Membership Committee

M.S. Epstein

National Capital Area Skeptics, Board of Directors (Vice President)
Society for Scientific Exploration Annual Meeting, Program Committee
National Committee for Clinical Laboratory Standards, Subcommittee on Control of Preanalytical Variation in Trace Metal Analysis

Society for Scientific Exploration, Governing Council
Montgomery Area Science Fair (1993) (Judge)
Interagency Environmental Technologies Exports Working Group
NSTC-CENR Subcommittee on Environmental Technologies

J.D. Fassett
NCCLS Subcommittee on Trace Metal Analysis
SRM Process Improvement Team

R.R. Greenberg
ASTM, E010 Nuclear Technology and Applications
ASTM, SC.05 Nuclear Radiation Metrology
ASTM, WG.12 Nuclear Methods of Chemical Analysis
ANS, Trace Analysis Committee, Division of Biology and Medicine
ANS, Executive Board, Division of Biology and Medicine

W.R. Kelly
Sigma Xi Program Chairman

W.F. Koch
Analyst CSTL, NIST Program Office
NCCLS, C004 Board of Directors
NCCLS, C016 National Committee for Clinical Laboratory Standards
ASTM, D-19 Water
ASTM, D-22 Sampling and Analysis of Atmospheres
ASTM, SC.06 Acid Deposition
ASTM, WG.03 Ph in Atmospheric Deposition
ASTM, SC.02 General Specifications and Technical Resources
ASTM, SC.02 Clinical Standards
AWWA, C002 Standards Methods
AWWA, SC.05 Inorganic Constituents in Water
IUPAC, 005 Analytical Chemistry Division
IUPAC, C.05.5 Electroanalytical Chemistry

G.P. Lamaze
ASTM, E010 Nuclear Technology and Applications, Chairman
ASTM, SC10.95 Long Range Planning
ASTM, SC.05 Nuclear Radiation Metrology
ASTM, SC.94 Membership Subcommittee, Nuclear Technology and Applications
ASTM, E42 Surface Analysis

R.M. Lindstrom
National Steering Committee for the Advanced Neutron Source

J.R. Moody

ASTM, D-19 Water
ASTM, D-19.05 Inorganic Constituents in Water
ACS, C002 Analytical Reagents
IUPAC, 002 Inorganic Chemistry Division
IUPAC, SC.02.04 Isotopic Specific Measurements as References
ANSI, C098 US TAG(Technical Advisory Group) to ISO/TC 209 "Cleanrooms and Associated Controlled Environments"

P.A. Pella

ASTM, E001 Analytical Chemistry for Metals, Ores, and Related Materials
ASTM, SC22 Statistics and Quality Control

K.W. Pratt

ASTM, D-19.05 Inorganic Constituents in Water
IUPAC, Committee V-5 (Electroanalytical)

M.V. Smith

ASTM, E013 Molecular Spectroscopy
ASTM, SC.01 Ultraviolet and Visible Spectroscopy

G.C. Turk

IUPAC, Committee V-4 (Spectrochemistry)

T.W. Vetter

ASTM, E001 Analytical Chemistry of Metals, Ores and Realted Materials
ASTM, SC.01 Iron, Steel, and Ferroalloys
ASTM, SC.02 Ores, Concentrates and Related Metallurgical Materials
ASTM, SC.02.01 ISO Tag on Concentrates
ASTM, SC.21 Reference Materials and Liaison with S17
ASTM, SC.23 Terminology
ASTM, SC.24 Editorial and Publications

R.D. Vocke

IUPAC, Commission on Atomic Weights and Isotopic Abundances (CAIWA), Associate Member
IUPAC, Subcommittee on Isotopic Abundance Measurements (SIAM)
IUPAC, Subcommittee on Natural Isotopic Fractionation

R.L. Watters

CIPM, Consultative Committee on Amount of Substance
  Comité International des Poids et Measures(CIPM)
  Comité Consultatif pour la Quantite de Matiere (CCQM)
ASTM, E001 Analytical Chemistry of Metals, Ores, and Related Materials
ASTM, SC.01 Iron, Steel, and Ferroalloys
ASTM, SC.20 Fundamental Practices

ASTM, SC.24 Statistics and Quality Control
Cooperation on Inter-National Traceability in Analytical Chemistry (CITAC)

M.R. Winchester
Society for Applied Spectroscopy, Baltimore/Washington local Section, Delgate
ISO TC201 WG1, Glaw Discharge Spectrometry Working Group
U.S. Technical Advisory Group for ISO TC201 WG1 (ASTM E42.92.08)

9. Editorships

M.S. Epstein
Journal of Analytical Atomic Spectroscopy, Editorial Advisory Board
Journal of Scientific Exploration, Column Editor
CSTL Update Newsletter, Editor
Talanta, Editorial Advisory Board

P.A. Pella
X-Ray Spectrometry (News Editor)

G.C. Turk
Journal of Analytical Atomic Spectroscopy

10. Seminars

December 6, 1993
J.E. Denoyer, The Perkin-Elmer Corp., Wilton, CT, "Flow Injection and ICP-MS: Synergy and Implications." (Division Sponsor: M. Salit)

February 17, 1994
Laurie Bobyak Hackenberger, Pennsylvania State University, University Park, PA, "The Effect of Stoichiometry on the Phases Present in Boron Nitride." (Division Sponsor: G.P. Lamaze)

February 21, 1994
A. Prange, GKSS Research Centre, Geesthacht, FRG, "Trace and Microchemical Applications of Total Reflection X-Ray Fluorescence." (Division Sponsor: P. Pella)

11. Conferences/Workshops/Sessions Sponsored/Co-Sponsored

January 28, 1994

Workshop on Preparation of Secondary Reference Materials for Lead, National Institute of Standards and Technology, Gaithersburg, MD (J. DeVoe)

April 4-9, 1994

Workshop on Sustainable Development in Urban Areas of the Americas, Santiago, Chile (R.G. Downing)

July 5-6, 1994

Meeting of the CIPM Working Group on Metrology in Chemistry, National Institute of Standards and Technology, Gaithersburg, MD (B. Watters)

12. Faculty Appointments

Ronald F. Fleming, University of Michigan, Ann Arbor, Michigan

IV. Organic Analytical Research Division (835)

Willie E. May, Chief

A. Division Overview

The Organic Analytical Research Division is the National source for measurement science, reference materials/standards and related information pertaining to the characterization and quantitative analysis of organic compounds both pure and in complex matrices. The Division has a staff of approximately 40 scientists with research activities being carried out in four groups. *The Analytical Sensors and Automation Group* researches and implements new rapid and automatable approaches to organic analytical measurement including efforts in optical sensor design, flow injection immunoassay, capillary electrophoresis, supercritical fluid extraction technology, and laboratory robotics. *The Gas Metrology Research Group* conducts research directed toward the preparation and measurement of primary gas standards. The Group is the Nation's primary reference laboratory for quantitative measurement methods and gas standards for a broad spectrum of areas including the atmosphere, vehicle emissions, and hazardous waste sites where the gases range in concentration from the low percent to parts-per-trillion levels, and in complexity from single to multicomponent mixtures. The standards produced by the Group are recognized as being definitive by both industry and local, state, and federal regulatory agencies. *The Mass Spectrometry Group* conducts research on the development of definitive measurement methods for clinically significant analytes in serum, on the use of tandem mass spectrometry for quantitative analysis, on the application of mass spectrometry for structural determination of biomolecules, and on the development of methods for trace organic analyses of complex mixtures. *The Separation Science Group* conducts investigations regarding the molecular interactions that occur during chromatographic processes, the design of "tailored" stationary phases for specific applications, and the development and critical evaluation of new approaches for the separation, detection, and quantitation of individual organic constituents in complex matrices.

The Division's FY94 research and service programs were supported through four primary sources: nearly half from the NIST Congressional appropriation, which supported fundamental research and measurement activities in trace organic analytical chemistry and gas metrology; slightly more than one-fourth from reimbursements for research and measurement activities conducted in support of other Federal and State Agency programs; nearly one-fifth from measurement activities conducted in support of the NIST Standard Reference Materials Program, which resulted in the certification of 57 SRM/RMs; the remainder from other research, measurement and service activities undertaken on a cost-reimbursable basis in support of U.S. industry.

Organic analytical chemistry continues to be a fertile research discipline that is critical to maintaining and improving public health, food/nutrition, the environment, and U.S. industrial competitiveness. Scientists in the Division are making significant contributions to the development, theoretical understanding and application of new and emerging chemical measurement technologies such as analytical sensors, capillary electrophoresis, flow injection immunoassay, supercritical fluid and microwave-assisted solvent extraction technology, and laboratory automation, while maintaining world-class capabilities in the chromatographic sciences, laser spectroscopy, organic mass spectrometry, and gas metrology. The development and maintenance of these and other measurement technologies are vital to achieving and maintaining a world-leadership position in organic analytical measurement science. Descriptions of many of the Division's research activities are provided in the Technical Activities Section that follows.

Other Federal and State Government Agencies continue to be important customers of the Division. During the past year, we were involved in 18 projects with 10 Federal and State Government Agencies. As in the past several years, our two largest Other Agency programs were based on providing analytical measurement quality assurance (QA) support for (1) epidemiological studies and cancer chemoprevention trials conducted by the National Cancer Institute (NCI) and (2) marine pollution monitoring programs being undertaken by the National Oceanic and Atmospheric Administration (NOAA) and the Environmental Protection Agency (EPA). The NCI program serves over 70 laboratories world-wide, involved in studies to determine the efficacy of selected fat-soluble vitamins and other phytochemicals as cancer chemopreventive agents. The NOAA/EPA program provides analytical QA support to over 30 laboratories involved with the measurement of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and chlorinated pesticides in marine sediments and tissues. During the past year, our efforts in support of U.S. Army chemical warfare treaty verification activities continued to increase. Our laboratory-based activities were reduced, but our consultative efforts regarding measurement QA increased. Our consultative efforts were primarily associated with issues concerning instrumentation and technology for use during treaty-mandated on-site industrial inspections. The technology to be used must provide data of specificity sufficient to document compliance while minimizing access to industrially-sensitive and often proprietary chemical information.

Our direct interactions with U. S. industrial firms have increased dramatically over the past several years. As in the past, the majority of our efforts in this area have been directed toward interactions with consortia, professional, and/or industrial trade organizations. Four such interactions will be highlighted in the following paragraphs. The Consortium on Automated Analytical Laboratory Systems (CAALS) is headquartered at NIST and has nine U. S. - based corporations and two Federal Agencies as members. Over the past several years, research efforts within the consortium have been focused on the development of U. S. industry-wide automation compatible systems for chemical analysis. During FY94, CAALS underwent a major reorganization to better address the needs of its existing members and become more accessible to the laboratory automation community. The $30K annual membership fee, seen as a barrier preventing many companies from participating in the Consortium, was reduced to $2.5K. This drastic reduction in fee was made possible by new NIST funding from the System Integration for Manufacturing Applications program of NIST's FY94 High Performance Computing and Communications initiative. CAALS has also changed its focus from attempting to develop standards for the industry to one of facilitating and supporting the development of standards. A new CAALS CRADA was developed incorporating these changes and stating that all Consortium outputs would be in the public domain. This change in focus has resulted in several new companies joining the Consortium. Several of the new CAALS members are involved in clinical chemistry applications, therefore the Consortium will shift some of its efforts toward needs in this area.

The College of American Pathologists (CAP) is a professional organization comprised of over 1000 physicians who specialize in pathology. The CAP oversees the performance of clinical laboratories in the U.S. through a variety of activities, including the administration of proficiency testing surveys. Two CAP-sponsored Research Associates work along with Division staff to develop definitive measurement methods for clinically-significant analytes in body fluids and to apply this technology in the value assignment of SRMs used throughout the clinical measurement community as well as proficiency testing pools and reference materials used in CAP programs. Our FY94 activities were focussed on using NIST measurement technology for value assigning several serum-based CAP standards for glucose, cholesterol and triglycerides, and urine-based CAP Reference Materials for amphetamines and phencyclidine.

New vehicle emissions limits imposed by the Clean Air Act of 1990 will require vehicle manufacturers to develop more sophisticated analytical tools to demonstrate compliance. In FY94, the Organic Analytical Research Division supported U.S. automotive industry emissions reduction research efforts by developing two critical SRMs: a 0.25 ppm propane in air SRM to extend the NIST series of standards to the range needed for measuring hydrocarbon exhaust emissions from next generation vehicles; and a complex low-level volatile organic compound (VOC) mixture to evaluate various new technologies for measuring non-methane organic compounds. During the summer of 1994, representatives from Chrysler Corporation, Ford Motor Company, General Motors Corporation, Navistar International Transportation Corporation, the California Air Resources Board, and the U.S. Environmental Protection Agency met at NIST with management and technical staff of the Chemical Science and Technology Laboratory (CSTL) to discuss the new measurement technology and standards needs associated with the development of next generation "clean" U.S. automotive vehicles. CSTL agreed to establish a new program directed toward the "Development and/or Critical Evaluation of Technologies for the Real-Time Chemical Analysis of Automotive Exhaust". The program will consist of five projects:

- Vehicle Exhaust Flow Measurement Technology [Division 836]
- Microsensor Array Technology [836]
- Doppler-Free Infrared Polarization Spectroscopic Measurement Technology [835]
- On-Demand Generation and Delivery of Formaldehyde-in-Air Standards [835]
- Gas SRMs for Low-Emission Vehicles [835]

These projects are focussed primarily on U. S. Automotive Industry needs for new "Vehicle Exhaust Volume Measurement Technology, a "Fast Oxygenated Hydrocarbon Speciation Analyzer" and "Standard Reference Materials" to support emissions measurements from low-emission vehicles.

Standard Reference Materials development was again a major component of the Division's research, measurement and service programs. Research and measurement activities were directed toward the certification of 57 SRM/RMs of industrial, environmental, and/or health/safety importance. Additional details concerning all the SRM projects undertaken in

FY94 are provided in the Outputs and Technical Reports sections that follow. Here I will discuss only one of our government/industry driven standards programs to demonstrate the relevance and impact of our standards activities. According to EPA Administrator, Carol Browner, the expanded use of reformulated gasolines will reduce smog-producing car emissions in the U.S. by 305,000 tons next year. In that context, the Division worked with EPA, the California Air Resources Board, and the Western States Petroleum in the Division Association over the past year to develop standards for reformulated fuels. Work was completed on a suite of eight "Oxygenates in Gasoline" Standard Reference Materials required by Federal and California regulations to document mass percent of oxygen in all commercial gasolines. To extend the availability of these standards and to provide a defined traceable link through secondary standards producers, we also certified eight oxygenates-in-gasoline reference materials for a commercial reference material supplier through our new NTRM program. FY95 activities in this area include the development of a reformulated diesel fuel reference material and a synthetic gasoline material to be certified for benzene, total aromatic content, total oxygen content, total olefin content, and sulfur.

In addition to the SRM-related activities described above, the NIST traceable gas reference materials (NTRM) program continued to expand in FY94. This program was initiated in the fall of 1992 to address problems associated with both the availability and quality of the wide variety of cylinder based gas standards needed by the environmental monitoring community. The program allows Specialty Gas Companies to prepare NTRMs for any pollutant, concentration, and balance gas combination for which a NIST SRM or primary standards suite currently exists. The program requires that commercial suppliers of gas standards produce candidate NTRM cylinders in batches of 10 or more, provide NIST with data concerning batch homogeneity, and submit to NIST randomly selected cylinders from the batch for measurement. Based on both company and NIST measurement data, NIST provides value assignment and issues NTRM certificates for all cylinders in the batch. During the past year, 28 NTRM batches were prepared for three companies. Five companies have expressed interest in certifying approximately 50 NTRM batches in FY95.

International trade and increased requirements for quality systems documentation are demanding that NIST develop a more formal definition of "traceability" for chemical measurements. The evolving linkage between the U.S. and world economy has resulted in an increased awareness of the need for comparability among data used to assess feedstock and product quality and/or evaluate processes. A well-conceived and implemented NIST program for establishing traceability for chemical measurements on a worldwide basis is essential to promote U. S. interests in the world marketplace. During FY94, efforts were begun to conceptualize a chemical measurements traceability infrastructure with vertical and horizontal components. The vertical component would extend downward within the U.S. to encompass commercial producers of reference materials and the horizontal component would extend outward to include international metrology and standards institutes. The NTRM program described earlier is an example of a vertical traceability program. A similar program for calibration solution standards is being discussed. Formal collaborations regarding trace organic analytical metrology have begun with the Netherlands Measurement Institute, Centro Nacional De Metrologia (Mexico), and the National Research Council of Canada.

As stated previously, the work of the Division includes a broad range of research and service activities within the general areas of organic analytical chemistry and gas metrology. Programmatic activities include efforts directed toward health and clinical chemistry, food and nutrition, and the environment. Support of and collaboration with U. S. industry is on the increase. The Technical Highlights and Outputs and Interactions sections that follow provide details that reflect the high quality of the staff and broad impact of their contributions to NIST and the Nation.

During the summer of 1994, a decision was made to combine the Organic and Inorganic Analytical Research Divisions. The vision for the new Analytical Chemistry Division is to be recognized as the Nation's reference laboratory for chemical metrology and compositional analysis by providing traceability through measurement technology, reference materials, data, and services required to meet future science and technology needs. In this vision, the NIST Analytical Chemistry Division will play a leadership role in the critical evaluation, development and transfer of chemical metrology to facilitate international "free" trade, provide the analytical measurement infrastructure for sound business and environmental trade-off decision making, and quality systems documentation. Laboratory based efforts in this program would be in collaboration with other international chemical metrology institutes and the transfer standards would be developed, distributed and maintained at the leading metrology institute level--not sold commercially as are our SRMs.

The new Division's mission is to: conduct research concerning the qualitative and quantitative determination of chemical composition; develop and maintain state-of-the-art chemical analysis capabilities; provide measurement quality assurance through reference materials, data, and services; and provide a basis for U. S. chemical measurement traceability and international comparability.

At the beginning of FY95, the new Division will function as a linear addition of the two combined divisions. During the course of the year, a new organizational structure will be established as part of an overall NIST strategic planning process for analytical chemistry.

B. Selected Technical Reports
(Organic Analytical Research Division)

1. Progress on Developing the CAALS-I Communication Specification for Instrument-to-Controller Messaging

G.W. Kramer, S.F. Bostyn, M.W. Walter, and F.R. Guenther

Today, there are only a few fully automated chemical analysis systems (where raw samples go in and information comes out) because they are expensive and difficult to create. This stems principally from a lack of attention to and standards for the ways that instruments and controllers interact. The Consortium on Automated Analytical Laboratory Systems (CAALS) was created at NIST in 1990 as a partnership between Government and U.S. industry to seek ways around roadblocks to increased uses of automation in chemical analyses. Since instrument-to-controller interfacing and communications issues are paramount on the list of trouble points, CAALS has been developing a reliable and robust communication scheme for messaging. Over the past year this effort has produced the CAALS-I Communication Specification base document which will be issued as a NIST Internal Report. CAALS-I fully describes the protocol (communication rules) and syntax (message format) for instrument-to-controller communication; however, it specifies little about the semantics (content) of the messages.

CAALS-I is designed to provide platform-independent, guaranteed message delivery and connectivity across a variety of physical links. Currently, IEEE-488.1, EIA-232E, and Windows DDE (Dynamic Data Exchange) links are supported. CAALS-I makes maximal use of existing standards and provides a similar application programming interface across computing platforms that is independent of the physical link used.

Unfortunately, having just a paper specification like CAALS-I is not sufficient to ensure its adoption. To make CAALS-I as easy as possible for instrument manufacturers to utilize and embrace, this year we have completed a series of demonstration implementations of our specification that work on typical computing platforms used in analytical chemical instrumentation.

Demonstration software for both a controller and an instrument end has been developed using both the Windows and Windows NT environments. Instrument ends have been completed on V-25 and 8051 microcontrollers--two embedded processors typically found in small laboratory instruments. Additionally, a PC-based testing and validation tool for instrument-end implementations has been completed. During the upcoming year, we will be developing an implementor's guide for CAALS-I, addenda to the base document describing the demonstration implementations, and a generic ANSI C code kernel containing the protocol stack. The latter is an attempt to produce commercial quality code usable on a variety of platforms that can be incorporated directly into a manufacturer's product. CAALS documentation that has been released to the public is available on the CAALS anonymous ftp site (caals.nist.gov).

2. Determination of the Quantitative Potential of Electrospray Mass Spectrometry for the Determination of Proteins

D.M. Bunk and M.J. Welch

Clinical measurements require a high degree of specificity to ensure that the measured analyte response is due to the analyte and not a similar species that is inactive relative to the analyte. Assays of clinically-relevant proteins often lack high specificity because measurements are not made of the protein itself, but rather of a species whose abundance is related to the protein of interest, such as a tagged immunoglobin in an immunoassay. While these protein assay schemes can result in very high sensitivity, they are often obtained at the expense of selectivity. To obtain both sensitivity and selectivity in a protein assay, we have investigated electrospray ionization mass spectrometry (ESIMS) for the quantitation of proteins. ESIMS is a technique that involves generating a series of multiply charged ions from large molecules such as proteins. The pattern of charge states that results is a function of the size, structural components, and conformation of the molecule. Although ESIMS is routinely used for molecular weight determinations of proteins and for studies of protein conformation and non-covalent interactions, its potential for quantitative protein determinations has not been explored.

One of the first challenges in this research was finding a suitable internal standard. To match the ionization characteristics (i.e., the observed charge state distribution) of the analyte protein, the internal standard should be of a similar shape and size. Due to the mass resolving power of our mass spectrometer and the large molecular weights of the analyte, a 1% difference between the molecular weights of the analyte and internal standard is required for sufficient resolution. Based on these criteria, we chose protein from different animal species as internal standards; for example, for the quantitation of chicken lysozyme, we examined human, bovine, and turkey lysozymes as internal standards, all of which have slight variations in amino acid sequence, but overall a conformation similar to that of chicken lysozyme. Precision of ratio measurements of chicken lysozyme with the different species lysozymes varied considerably; additional experimentation indicated that this variability was due to differences in the adsorption of the different proteins on the tubing used to introduce the samples into the mass spectrometer. Solvent conditions were found which minimized protein adsorption. At this point, precision improved to 3-4% with all of the internal standards. Through these model studies with chicken lysozyme and human albumin, we have found ESIMS to produce a linear and reproducible response down to the low femtomole level of analyte protein. Because quantitative results are obtained along with an accurate determination of the protein's molecular weight, the selectivity of ESIMS is excellent. By coupling ESIMS with high-resolution capillary liquid chromatography, analysis of proteins in a complex matrix, such as serum or urine, can be performed. We are now investigating the direct determination of human albumin in serum by this approach.

While ESIMS lacks the speed and simplicity to replace current routine clinical protein determinations such as immunoassays, it can be used for the validation of these methods. With continued development, ESIMS will be a powerful tool for the preparation of protein reference materials, thus improving the accuracy of clinical diagnosis.

3. Development of Quantitative Tandem-in-Time MS/MS on an Ion Trap Mass Spectrometer

C.S. Phinney and M.J. Welch

Tandem mass spectrometry, or MS/MS, is a technique that provides added specificity to mass spectrometric analyses. Ion trap mass spectrometers that have this capability have the potential for high sensitivity as well as high specificity. The operating software for MS/MS on these systems is written to optimize the isolation and excitation of a single parent ion. The most accurate approach to quantitation by mass spectrometry involves use of isotope labeled internal standards. MS/MS, when an isotope labeled internal standard is included, requires the simultaneous isolation and excitation of two parent ions. We therefore undertook an investigation of various software-changeable parameters to determine if we could make the necessary modifications to perform quantitative MS/MS. As a test of the modifications, we investigated the determination of 11-nor-delta-9-tetrahydrocannabinol-9-carboxylic acid (THC-9-COOH) in urine. We then used this method to confirm GC/MS results for this compound in SRM 1511, Multidrugs of Abuse in Freeze-dried Urine.

Determination of THC-9-COOH is a standard procedure for drug testing laboratories, since this compound is the primary metabolite found in urine after marijuana use. The primary measurement technique for THC-9-COOH in SRM materials employs quadrupole GC/MS, and is a reliable and accurate method. The second method utilized HPLC with UV detection, but this method was very difficult to reproduce for different materials. We therefore undertook development of a GC/MS/MS method that differed from the primary method in terms of sample preparation, MS instrumentation, and analytical scan functions.

The Finnigan Ion Trap Mass Spectrometer is configured with a Selective Mass Storage option, and tandem-in-time experiments were performed using Ion Catcher Mass Spectrometer (ICMS) software developed by R. Yost and N. Yates at the University of Florida. The standard ICMS MS/MS scan functions were modified to allow two-step isolation of the range of masses corresponding to the electron impact base peaks of THC-9-COOH and THC-9-COOH-d_3 trimethylsilyl (TMS) derivatives, i.e., $m/z = 371\text{-}374$. Subsequent broadband excitation of these isolated ions resulted in collision-induced disassociation formation of daughter ions at m/z 305 and 308 for the unlabeled and labeled forms, respectively. Initial measurements of the ion intensity ratios of the daughter ions produced values with unacceptably poor precision. Careful evaluation of potential sources of variability led to the conclusion that the ICMS frequency modulation pattern was too narrow to provide uniform excitation across the 3 amu parent ion window. The frequency modulation pattern was then modified to generate a broader range of excitation frequencies, resulting in relatively equal and stable disassociation energies for both parent ions.

For the analysis of THC-9-COOH, commercial solid-phase extraction columns for urinalysis were used to separate the analyte from the sample matrix. The THC fraction was eluted, blown down to dryness, and taken up in N,O-bis(trimethylsilyl)acetamide (BSA) to form the TMS derivatives. These TMS derivatives were analyzed directly by GC/MS/MS. The GC/MS/MS mean value for four samples was 14.0 ng/ml, in excellent agreement with the GC/MS mean value of 14.1 ng/ml. These results demonstrate that this technique can be a valuable tool for accurate trace organic analysis.

4. Completion of the Certification of SRM 1511, Multidrugs of Abuse in Freeze-dried Urine

R. Christensen, P. Ellerbe, C.S. Phinney, L.C. Sander, S. Tai, and M.J. Welch

Drug abuse continues to be a major problem in the United States. To identify users of illegal drugs, drug testing programs are widely used in pre-employment, on-the-job, and criminal justice situations. Most of these programs follow a two-step process to ascertain drug use. First urine samples are screened, usually by an immunoassay procedure. Those that give a positive response above a cutoff level are then subjected to confirmatory testing by gas chromatography/mass spectrometry (GC/MS). This testing step is used not only to verify the presence of a controlled substance in the urine, but also to determine its concentration. If the level is above the specified cutoff level, the sample is reported as a positive. If the drug is absent or is found to be below the cutoff, the sample is reported as negative. Thus, it is very important for drug testing laboratories to perform accurate quantitation, particularly in the region near the cutoff concentration.

NIST, working with the College of American Pathologists (CAP), has developed a series of urine-based SRMs and CAP RMs for the seven substances that must be tested for as part of Federal Workplace Drug Testing Program. Each of these materials consists of three levels of one or two of the controlled substances. Many SRM customers requested a single material that contained all of the mandated substances at their respective cutoff levels. To meet this need, SRM 1511, Multidrugs of Abuse in Freeze-dried Urine, was commercially prepared with seven components having concentrations within 10% of their cutoffs. Several new methods had to be developed at NIST so that measurements of each analyte were performed using two different methods. For the marijuana metabolite, the two methods involved GC/MS and GC/MS/MS (see Technical Highlight # 3). For the other six compounds, the two methods involved GC/MS and liquid chromatography/mass spectrometry (LC/MS). Because very good agreement was achieved between the two methods for five of the analytes, benzoylecgonine (cocaine metabolite), marijuana metabolite, morphine, codeine, and phencyclidine, their concentrations were certified. Unfortunately, the results for amphetamine and methamphetamine concentrations showed a significant decline over time, so these analytes were not certified.

SRM 1511 should meet many of the needs of drug testing laboratories for assuring the accuracy of their GC/MS methods in the cutoff region. Laboratories needing reference materials for the amphetamines can obtain such a material from CAP that was certified at NIST. As with similar SRMs, NIST will continue to monitor the stability of SRM 1511 in future years.

5. Development of Isotope Dilution/Gas Chromatography/Mass Spectrometry Methodology for the Determination of Fatty Acids in a Composite Food Material

M.J. Welch

A number of forces are driving the U.S. food industry to provide more accurate and complete labeling of foods. Legislation has been enacted that requires much greater labeling of foods than before; foreign countries are requiring better documentation on foods they import, and nutritional studies are investigating which components are responsible for healthful and harmful effects of certain foods. All studies of U.S. food consumption patterns agree that most Americans consume too much fat. High fat and cholesterol consumption increases the likelihood of heart disease, stroke, and certain forms of cancer. However, some studies have found that certain fats are more harmful than others. Consequently, a complete nutritional assessment of the fat content of a food requires an analysis of the fatty acids that make up the fat. While there are a number of methods for determining the fatty acid content of solid and liquid fats, little work has been done on determining the fatty acid content of other foods. Furthermore, there is a serious lack of reference materials available to the food industry to validate their measurements for many important food components.

To address this need, NIST and USDA are jointly developing a new material, SRM 1544, Fatty Acids in a Food Composite. This material is a blend of many different foods representative of a typical U.S. diet. It was prepared under the direction of USDA, which then bottled the material and stored it at -70 °C. Measurements of the cholesterol level in this material were performed at NIST using the isotope dilution (ID) GC/MS definitive method for cholesterol, which had been used for other food-based SRMs. Fatty acids had not been measured in foods previously at NIST. Existing GC methods in the literature were modified for ID/GC/MS and tested. Results were unsatisfactory until modifications were found that produced reproducible results. In our method, the fatty acids are extracted from the matrix prior to conversion to their methyl esters. Efforts focused on the four most abundant saturated fatty acids (C-12, C-14, C-16, and C-18) and the two most abundant unsaturated fatty acids (oleic and linoleic). Results for the saturated fatty acids were quite reproducible, but were somewhat more scattered for the unsaturates. These results will be compared with those from the second method, a conventional GC analysis performed at USDA. This method uses a different polarity GC column and a different derivatization reagent and procedure. If the results from the two methods are in satisfactory agreement, the concentrations will be certified.

SRM 1544 will also have information values on a number of other nutritional components, based upon analyses performed at several large commercial laboratories. This material should be a valuable traceability tool for the U.S. food industry.

6. Supercritical Fluid Extraction as a Forensic/Clinical Tool; The Extraction and Detection of Drugs-of-Abuse in Hair

J.F. Morrison and W.A. MacCrehan

In recent years human hair has received considerable attention as a toxicological specimen for evidence of chronic drug use in clinical and forensic investigations, as well as in pre-employment and employee drug testing programs. Compared to urinalysis, hair analysis has the potential for greatly expanding the time window of drug detection, sample acquisition is less invasive, and the hair specimen is less subject to purposeful adulteration. Despite these advantages, widespread acceptance of hair as a reliable drug testing medium has been hindered in part by our limited understanding of the mechanisms of drug incorporation in hair, a lack of uniformity in analytical hair drug testing protocols, and continued controversy over the effectiveness of current procedures for distinguishing a true positive result from a false positive which may arise due to environmental drug contamination of the hair sample (i.e., passive exposure).

A new method based on supercritical fluid extraction (SFE) technology has been developed in our laboratory for the rapid, efficient recovery of cocaine from hair. The method employs supercritical carbon dioxide modified with microliter amounts of water and triethylamine as the extractant phase. Quantitative extraction of cocaine is achieved in less than forty minutes with little sample manipulation, providing a significant reduction in sample preparation time compared to currently used labor- and time-intensive wet chemical extraction procedures (several hours to 1 day). Additionally, we have taken advantage of the inherent selectivity of the SFE technique to distinguish external drug contamination from active drug use, since drug present on the surface of hair due to passive exposure is recovered under dramatically different SFE conditions than drug incorporated within the hair matrix due to drug use. A two-step SFE procedure is currently being evaluated which involves (1) recovery of external drug contamination using pure carbon dioxide, followed by (2) recovery of incorporated drug using carbon dioxide modified with water and triethylamine.

The NIST SFE research has been well-received by the hair drug-testing community. A strong collaboration has been established with National Medical Services, Inc., one of the largest commercial hair drug testing laboratories in the U.S., to allow further development and commercialization of the SFE technique. On-going research involves fundamental studies of the influence of the hair matrix on drug extractability in order to investigate analyte-matrix bonding mechanisms and differentiate discrete sites of interaction. Preliminary studies have also begun on the feasibility of interfacing SFE with immunoassay formats to provide rapid, automatable drug screening methods for forensic and clinical laboratories.

7. Identification of Explosives Residues by MECE with Zone-Focussing

K.D. Smith and W.A. MacCrehan

NIST has been working in close collaboration with FBI and George Washington University researchers to extend the use of Micellar Electrokinetic Capillary Electrophoresis (MECE) for forensic identification of explosive residues. Past work demonstrated the concept of MECE detection of the characteristic compounds that are blended into gunpowders, including propellants, stabilizers, burn rate modifiers and plasticizers. About 25 of these neutral organic molecules can be separated using a charged detergent in the capillary electrophoresis system in under 15 minutes. Using MECE, a pattern of occurrence can be determined, revealing components common to the unfired gunpowder and crime-scene residues providing evidence to support a criminal investigation.

One important part of the new work was to investigate the use of "zone-focussing" to improve the efficiency and resolution of the MECE separation. Addition of a zwitterionic surfactant, sulfobetaine (SB-12), to the sample caused an increase in the separation efficiency of the more highly retained components. We initially investigated this effect by varying the amount of SB-12 added to the sample. We also found the focussing effect occurs when a short "plug" of SB-12 is injected into the capillary before the sample. We have investigated the influence of SB-12 concentration, plug length and delay time on the efficiency and signal intensity of 5 test residue components. In optimum cases, the efficiency has increased from 250,000 plates to over 1,000,000 plates for late eluting components on a 75 cm column. Additional benefits include a twofold increase in peak areas and a more rapid equilibration of the capillary to the buffer system than without SB-12. We are currently trying to develop a model to explain this focussing effect and test it on real residue samples.

In the past year, we also examined sampling protocols for gunpowder residues from both firearms use and pipe bomb blasts. The FBI provided NIST with a series of test bomb fragments from known gunpowders made by field detonations and trapping of the pipe fragments in a coiled chain link fence. Test gunshot residue targets were provided by the Armed Forces Institute of Pathology and deliberately contaminated with blood, grease, and sweat. We investigated 2 methods of collecting the residue particles - swabbing with alcohol and lifting with masking tape. Three methods were tested for dissolving the characteristic components from the lift samples for MECE analysis: (1) complete dissolution of the nitrocellulose matrix in acetone followed by precipitation with run buffer (2) leaching of the soluble components in alcohol and (3) supercritical fluid extraction (SFE) using carbon dioxide modified with acetone. Positive results can be obtained for gunshot residues with the tape lifts, but swabbing produced better results for the bomb fragment residues. The SFE technique gave the cleanest extracts for MECE determination. Recently, we shared the results of these studies with the FBI and performed a field demonstration of the MECE method at their Quantico research laboratory.

8. FT-NIR/Raman Identification and Quantitation of Oxygenates in Ampouled Gasoline

S.J. Choquette, D.L. Duewer, R.G. Christensen, and S.N. Chesler

Oxygen additives, such as ethanol, methyl t-butyl-ether, ethyl t-butyl ether, tertiary amyl-methyl-ether, and methanol are commonly mixed with gasoline to reduce automotive emissions. As the EPA regulates minimum oxygen levels, the petroleum industry requires accurate methods and standards by which to measure them. Currently, gas chromatography (GC) and FT-IR spectroscopy are the methods used for quantitation; however, these methods are time consuming, and typically destructive (GC). In addition, the volatility of the sample makes quantitative analysis difficult. We are investigating the use of FT-near infrared spectroscopy (NIR) and FT-Raman Spectroscopy for the nondestructive, real-time evaluation of oxygenates in ampouled gasoline. Due to the lower extinction coefficients in the near-IR, transmission measurements may be readily made through the 25 mm diameter SRM ampoules. Our current project will evaluate NIR and Raman as potential quantitative spectroscopic methods for the determination of all four oxygenates at the 0.1% (w/w) level in a commercial reference gasoline. The goal will be to establish whether either or both techniques may be used as a real-time process technique for measuring oxygenate levels in SRM ampouled gasoline samples.

In the initial study, a training set of 80 samples of gasoline containing the four oxygenates was used to evaluate the NIR and Raman methods. Each sample contained only a single oxygenate present in 1 of 2 different concentrations. The spectra from this training set were then analyzed using a partial least squares multivariate calibration technique. Individual samples from the training set, as well as samples external to this set were then analyzed based on the calibration model. The results showed that we could successfully identify the four oxygenates, using either spectroscopic method to within 0.5% of the oxygenate value determined by GC. We are currently optimizing the calibration procedures combined with novel sampling geometries to obtain the desired accuracy. Future areas to be considered will be the use of more robust statistics, transfer of calibration curves (between instruments), mixed oxygenate quantitation and identification, and speed of analysis.

9. Homogeneous Flow Immunoassay for Measuring Serum Cancer Markers

L. Locascio-Brown, R.G. Christensen, and S.J. Choquette

The ongoing development of flow injection immunoassays for the measurement of serum cancer markers has this year been marked by intense public and industrial interest due to its application to breast cancer assessment. A joint patent was allowed in early 1994 on the generic technology which involves the use of liposomes as amplification reagents in a solid phase flow immunoassay scheme. The Flow Injection Liposome Immunoassay (FILIA) has been modified this year to accomplish the simultaneous determination of two and three estrogen metabolites as a method that can be used to potentially screen serum samples for the presence of a breast tumor. This measurement is being done to support research efforts at Strang-Cornell Hospital (NY, NY) which indicate that the appearance of an abnormal breast cell is strongly linked to a pronounced change in the metabolic pathway of the parent estrogen, 17-β-estradiol. The first assays were performed in FY94 for measurement of estrogens using a solid phase immobilized estrogen, and a liposome label which incorporated the appropriate estrogen antibody on the surface. The assay was performed by mixing the estrogen in serum samples with the immunoreactive liposomes, followed by injection into the solid phase reactor. Bound liposomes were quantitated by fluorescence detection of liposome-encapsulated dye following liposome rupture with detergents. The two and three estrogen assays were achieved using different fluorescent dyes encapsulated in liposomes to represent each individual species. Detection limits using alternate fluorophors were higher than required due to lower quantum efficiency and solubility of these dyes in buffers of physiological pH.

All assays previously described by us represent traditional solid phase immunoassays. In this type of assay, the immunoreactive species is bound covalently or noncovalently to the solid phase for separation and subsequent quantitation of the analyte. The throughput of these systems is low due to the additional time required for regeneration of the immobilized species for further analysis. We are currently developing a new approach to performing flow immunoassays in order to simplify the procedure by eliminating the need for immobilized immunoreagents. In this flow system, a competitive fluorescence immunoassay is performed in solution, and the resulting mixture is passed through a commercially available solid-phase extraction column for separation and identification of analyte concentration. The method is currently being used to quantitate drugs in serum, and is being explored as an alternative to previous assay designs for measuring estrogens since it is inherently a much simpler, faster, and less expensive method of analysis.

10. Analysis of *Oleoresin Capsaicin* Content of Hot Pepper Sprays by LC/MS

R.G. Christensen

Oleoresin capsicum (OC) is a component of some commercially-available sprays used to incapacitate violent persons. Since it is a natural product, an extract of hot peppers, its composition is variable. The National Institute of Justice and the Office of Law Enforcement Standards are interested in objective ways of assigning some quantitative scale of effectiveness to sprays based on this preparation.

The pungency of taste of capsaicinoid compounds is usually assigned a measure in Scoville Units (SU). This is the dilution at which they can be barely detected by a trained taster. A survey of the literature suggests that the pain produced by the various compounds may not be proportional to the pungency in SU. One investigator gives "mean pain potentials" (MPP) for various capsaicinoids. Another possible measure is merely the sum of the concentrations of the active compounds present.

A liquid chromatographic separation was developed, using thermospray LC/MS to identify the peaks attributable to the five major capsaicinoid compounds present in the preparation. Quantitative estimates of their concentrations were made by liquid chromatography using detection by ultraviolet absorbance. From these concentration measurements, using published MPP and SU values for pure compounds, three figures of merit were calculated: SU, an analogous "Pain Index" based on MPP, and the simple sum of capsaicinoid concentrations. The calculated SU values agreed well with the SU values given for preparations submitted for analysis, and there seemed to be a good correlation of them with the calculated Pain Index values and the sums of capsaicinoid concentrations. Any of the proposed figures of merit should be adequate for the intended purpose. It was also found to be possible to detect the presence of the possible synthetic adulterant, nonivamide, when present in an OC preparation.

11. Intercomparison of Primary Gas Standards with European Standards Laboratory

W.D. Dorko and F.R. Guenther

In July 1994, a memorandum of understanding was signed between NIST and the Netherlands Measurements Institute (NMi) located at Delft, The Netherlands. This agreement lists the terms and conditions of an intercomparison study to be carried out between the two institutes on Primary Standard Gas Mixtures (PSMs). One goal of the study is to enable a declaration of equivalence to be signed stating that certain PSM suites are equivalent, paving the way for traceability links between the United States and Europe. Another equally important goal is to help verify the validity of the two institutes' primary gas standards by cross checking of analyzed values. Another possible benefit would be gained if each national standards laboratory were to specialize in certain standards, thus eliminating the need to stock those standards at other national standards laboratories. This would allow scarce resources to be redirected to generate the new standards needed by industry worldwide. The agreement formalizes a working relationship that dates back to 1990.

Some terms in the agreement are: 1) PSM suites are to be intercompared on a regular basis. If PSM suites agrees to within previously defined statistical limits (usually 0.5 to 1.0%), they will be declared as equivalent. 2) PSM suites that do not agree within these statistical limits will not be declared as equivalent and will be the subject of additional bilateral work to identify and eliminate sources of bias. 3) A list of PSM suites declared to be equivalent will be published in a Annex to the Declaration of Equivalence document. A new Declaration of Equivalence shall become in force on July 1 of each year and will include an updated Annex listing. 4) Each party will inform the other of any anticipated circumstances that might impact the production and/or quality of PSMs.

The initial PSM suites to be studied are: SO_2, NO, H_2S, Propane, O_2, CO, and CO_2. Studies already undertaken in previous years have found certain PSM suites to be equivalent.

12. Development of Oxygenates in Gasoline Standard Reference Materials

S.N. Chesler and T.L. Green

Legislation was enacted in 1990 by the Federal Government and the State of California which requires a significant reduction in automobile exhaust emissions during this decade. As many studies have shown, the composition of automobile exhaust is directly related to the composition of the gasoline used. Thus, a major pathway to the mandated reduction of automobile emissions will be by re-formulation of gasoline. The addition of oxygenated hydrocarbons, usually in the form of aliphatic ethers, can significantly reduce hydrocarbon and carbon monoxide emissions. The addition of 15% of methyl t-butyl ether to commercial unleaded gasoline, resulting in a total enrichment of oxygen content by 2.7 mass percent, has been shown to lower the hydrocarbon and carbon monoxide emissions by 6 and 11 percent respectively.

Federal and California regulations will shortly require that all commercial gasoline contain 2.7 and 2.0 mass percent oxygen, respectively. In order to meet these oxygen content requirements, refiners will be blending aliphatic ethers and/or ethanol into unleaded gasoline feed stock at level of between 10 to 15 mass percent. A number of single ethers and/or ether mixtures will probably be employed, the most common materials being methyl t-butyl ether (MTBE), ethyl t-butyl ether (ETBE), and t-amyl methyl ether (TAME). Analytical methods for the determination of ethers within a complex hydrocarbon mixture are not trivial and require calibration through the use of accurate chemical standards. The California Air Resources Board (CARB), Western States Petroleum Association (WSPA), ASTM Committee D-2 and the Energy Resources Council (ERC) all have requested that NIST should undertake the development of suitable Standard Reference Materials (SRM). Eight oxygenate in reference gasoline solution SRMs have been prepared and certified during the past year.

Preparation of these materials was performed under contract by Scott Specialty Gases Inc. at their facilities in Houston, TX. The reference gasoline was obtained from Phillips Petroleum, Bartlesville, OK. The solutions were prepared by additive weighings of the oxygenate and the reference gasoline. After preparation and homogenization, the solutions were aliquoted into 20 mL glass ampoules which were subsequently flame sealed The certification measurements were based upon a statistical combination of the values obtained from gravimetric weighings and a gas chromatographic analysis. The final SRM package will include 1 ampoule containing blank gasoline and two ampoules containing the oxygenated gasoline at the certified level.

13. New Measurement Technology for Real-Time Analysis of Oxygenates in Automotive Exhaust

R.L. Sams and B. Mittermaier

The Automotive Industry/Government Emissions Research (AIGER) consortium has identified the real-time analysis of oxygenated species in automotive exhaust as one of their highest priority research goals. To address this need, NIST has initiated a program to assess the feasibility of using Tunable Diode Laser Adsorption Spectroscopy (TDLAS) and long path gas cells to collect quantitative spectroscopic data in real-time.

During the past year, spectrum of several of the oxygenates, methanol, ethanol, formaldehyde, acetaldehyde, acetone, methyl t-butyl ether (MTBE), t-amyl methyl ether (TAME) and ethyl t-butyl ether (ETBE), were taken on the Bruker FTIR at 0.11 cm^{-1} resolution. These spectra were evaluated for appropriate bands to study with the TDLAS system. Band strengths of most of the strong bands of MTBE, TAME, and ETBE from 4000-600 cm^{-1} were measured using up to

35 different pressure path lengths. The absorption coefficients for about 40000 different wavelength intervals were evaluated from the 35 different pressure path lengths.
Initial studies with the TDLAS system were with methanol and formaldehyde. The detection of formaldehyde was straight forward with a measured limit of detection of about 0.1 ppb. Methanol and the other oxygenates are more difficult to measure with the TDLAS system because the density of transition is too high, and doppler resolution is not sufficient to resolve them. The limit of detection for methanol was measured at about 50 ppb. Molecules as heavy or heavier than ethanol have too many overlapping transitions, even at doppler resolution, to be good candidates for TDLAS.

Since TDLAS is not suitable for the larger molecules of interest to the AIGER consortium, and because it was desired that the instrument not use liquid nitrogen, we have developed a new approach to solving the problem. Polarization spectroscopy has been used since the late 70's to make doppler free detection of molecules in the visible region of the spectrum. With the development of room temperature diode laser technology working at 1650 nm, it is now possible to exploit this technique in the near IR. It is a highly sensitive ($<10^{-8}$ absorbance units) and selective technique with resolution limited by the line width of the laser and pressure broadening effects. With the better resolution, an effective increase of around 1000, it will be possible to measure the larger oxygenates in the 1650 nm region. Even though the line strengths in this region are a factor of 10 to 100 smaller than the strong fundamentals, this should be strong enough to make this a viable technique. The polarization technique promises to be much more specific than TDLAS because of the capability to do sub-Doppler spectroscopy.

Over the next year, we will construct a Doppler Free Detection Instrument and determine the feasibility of using this instrument to measure oxygenates in real time, which the AIGER members can use in their test-bed environment.

14. Development of an Independent Calibration Method for Low ppm NO Gas Standards

W.J. Thorn III and G.H. Denny II

NIST currently provides nitric oxide (NO) in nitrogen Standard Reference Materials (SRMs) at 5, 10, and 20 μmol/mol to the mobile source measurement community for calibration of NO/NO_X exhaust emission monitors. The American automobile manufacturers, in response to clean air regulations, are building lower emission vehicles to reduce pollutants such as NO_X, and therefore will likely require lower concentration nitric oxide SRMs in the near future. There have already been inquiries into the feasibility of NIST supplying a nitric oxide in nitrogen SRM at 1.0 μmol/mol.

The certification of these lower concentration nitric oxide SRMs has always been a challenge because NIST's nitric oxide gravimetric primary standards do not go below 30 μmol/mol. Precise dynamic dilution of higher concentration SRMs and primary standards has provided the principal in-house reference mixtures against which the 5, 10, and 20 μmol/mol standards have been value assigned. This methodology has limited our concentration uncertainty estimates to ± 2 percent relative, with larger uncertainties as the NO concentration goes lower.

A low-nitric oxide calibration system has been developed which uses nitrogen dioxide (NO_2) weight loss through a permeable membrane as the NO_X primary standard. The new method provides known concentrations of nitrogen dioxide in nitrogen between the range of 0.25 and 30 μmol/mol at flow rates of 0.5 to 2 L/min. The NO_2 gas mixture is efficiently converted (disassociated) to a known NO concentration, which is used to value assign nitric oxide SRMs with a day-to-day uncertainty of ± 0.6 percent relative.

In the current study, five NO_2 permeation tubes were maintained in a water-cooled glass condenser at 23.00 ± 0.01 °C under a continuous flow of high purity nitrogen. The tubes were weighed on a microbalance every six days. Plots of permeation tube weight vs. elapsed time were developed for each tube resulting in second order polynomials for each of the five curves. The first derivative of these equations yields the instantaneous permeation rate of NO_2 in micrograms per minute for any specified elapsed time. An elapsed time was computed for every NO_X SRM measurement which allowed the permeation rates to be computed in micromoles per minute. The division of the permeation rate by the nitrogen flowrate yielded the standard NO_2 concentration in the calibration stream. An ambient chemiluminescent $NO/NO_2/NO_X$ monitor was modified to operate under positive controlled mass flow. A stainless steel thermal converter was placed ahead of the normal catalytic converter to achieve 99.9 + percent NO_2 to NO converter efficiency. NO_X response ratios of unknown NO gas mixtures to the generated NO_2 permeation standards were reproducible with an uncertainty of ± 0.2 percent relative.

NIST nitric oxide SRM lot control standards at 5, 10, and 20 μmol/mol were analyzed against the new permeation standard system yielding concentration values which agree within ± 0.5 percent relative to previously assigned concentration values. This observation validates this system's current performance which can be further improved with future modifications.

15. Technology for On-demand Production and Delivery of a Formaldehyde in Air Standard

R.L. Sams and W. J. Thorn III

The Automotive Industry/Government Emissions Reaserch (AIGER) consortium has identified formaldehyde standards as one of their high priority items for the next year. The Gas Metrology group has been studying formaldehyde for the past 3 years. This work was initiated under a CRADA with Motor Vehicle Manufacturers Association. Under the CRADA, NIST developed methanol-in-nitrogen primary standards and studied formaldehyde standards. Formaldehyde has been observed to be unstable in gas cylinders, and formaldehyde permeation tubes have been shown to be unreliable. In addition, the AIGER members have expressed reservations about having a full, pressurized, cylinder of this substance in their test-bed environment. Thus, we began developing a different approach using catalytic conversion of methanol to formaldehyde. We are confident that we can produce stable methanol in nitrogen standards; if we can develop a conversion method with 95% or greater efficiency, we will have solved the formaldehyde standards problem.

The tunable diode laser absorption spectrometer (TDLAS) system was used to monitor the conversion of methanol to formaldehyde. The initial work was done using 50 ppm methanol in nitrogen, 45.9 ppm methanol in air and 64.4 ppm methanol in nitrogen cylinder standards as the methanol sources, and silver wool, MoO_3, Fe_2O_3, and MnO_2 as catalysts. The methanol mixtures were flowed over the catalysts at different temperatures and into the long-path cell of the TDLAS system. The TDLAS system was set near the frequency of a strong formaldehyde transition which was selected to be near a CH_4 transition. The ratio of the formaldehyde transition to that of the methane was used as the multiplicative factor when comparing the unknown formaldehyde concentration to that of a methane. The concentrations of CO and CO_2 were measured using a second diode laser and gas SRMs. The preliminary results are as follows: 1) MoO_3 plus Fe_2O_3 resulted in approximately 55% conversion efficiency of methanol to formaldehyde. 2) The MnO_2 converted all of the methanol (100%), however, no formaldehyde was produced. 3) Best results were obtained with silver wool plus MoO_3 which gave conversion rates of from 80-86% formaldehyde with 3-6% CO_2 and 1-3% CO at a catalyst temperature range from 400-450 °C. The rate of flow in these initial experiments was 1-2 L/min. Flowing faster than 2 L/min resulted in a degradation of the conversion efficiency, probably due to the small amount (<100 g total) of the catalysts used in these experiments.

More work will be done to determine if the results are reproduceable over time and if there is any activation required after sitting idle for a period of months. We will also investigate other catalyst compositions to find the most efficient conversion rate. We will then develop a complete model of efficiency versus the operational parameters, to predict the formaldehyde concentration from the concentration of the methanol gas standard.

16. Certification of Three Mussel Tissue Reference Materials for Organic Contaminants

M.M. Schantz, B.J. Koster, D.L. Leister, and S.A. Wise

Standard Reference Materials (SRMs) are used by many laboratories to validate analytical procedures and to continuously monitor these procedures to verify that they remain in control. Four years ago, NIST issued the first tissue SRM for organic contaminants, SRM 1974 [Organics in Mussel Tissue (*Mytilus edulis*)] with certified concentrations for 9 polycyclic aromatic hydrocarbons (PAHs) and noncertified concentrations for 19 additional PAHs, 13 polychlorinated biphenyl (PCB) congeners, 9 chlorinated pesticides, and 36 trace elements. SRM 1974a was issued as a frozen tissue homogenate, rather than a freeze-dried matrix as most tissue reference materials, to be similar to the marine tissue matrices typically analyzed. Because of the widespread use of SRM 1974, the supply was depleted in 1993. A replacement material has been prepared and bottled as SRM 1974a. One goal for the reissue of the new mussel tissue material is to provide certified concentrations for a larger number of PAHs, as well as for a number of PCB congeners and chlorinated pesticides.

Prior to the blending of SRM 1974a, approximately 24 kg of the frozen mussel tissue homogenate was set aside for preparation of a second mussel tissue material, SRM 2974, which will be issued as a freeze-dried matrix. The freeze-dried mussel tissue was prepared to make it more accessible (i.e., easier shipping and storage), particularly for laboratories outside the U.S., and to assess the users' preference for frozen versus freeze-dried matrices. NIST is also participating in the preparation and certification of a third mussel tissue reference material in cooperation with the Group of Experts on Standards and Reference Materials (GESREM). This material, which will be issued as reference material (RM) 8045, GESREM II mussel tissue, is a freeze-dried mussel tissue and is intended for use primarily in developing countries.

The three mussel reference materials have been analyzed for PAHs using two analytical techniques; gas chromatography with mass spectrometric detection (GC-MS), and liquid chromatography with fluorescence detection (LC-FL). The three materials have also been analyzed for PCB congeners and chlorinated pesticides using three analytical techniques: GC with electron capture detection (GC-ECD) on two stationary phases with differing selectivity for these compounds and GC-MS. In addition, RM 8045 will be analyzed by the Marine Environment Laboratory, International Atomic Energy Agency, Monaco to provide additional measurements for the PAHs, PCB congeners, and chlorinated pesticides.

The results from the different analytical techniques will be combined to determine the certified concentrations. Each of the three materials will have certified concentrations for 15-20 PAHs, 15-20 PCB congeners, and 10-15 chlorinated pesticides, thus making these three materials the most well-characterized tissue reference materials available for the determination of organic contaminants.

17. Quality Assurance Activities for Determination of Organic Contaminants in the Marine Environment

R.M. Parris, M.M. Schantz, M.S. Cassedy, and S.A. Wise

NIST provides a variety of activities in support of environmental monitoring programs for organic contaminants. The largest of these programs has been funded for the past eight years by the NOAA National Status and Trends Marine Monitoring Program and the EPA Environmental Monitoring and Assessment Program. For this program, NIST efforts focus on providing mechanisms for assessing the interlaboratory and temporal comparability of data, and on improving measurements for the monitoring of organic contaminants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl congeners (PCBs), and chlorinated pesticides in bivalve, sediment and fish samples. This program includes the development of improved analytical methods, production of needed NIST Standard Reference Materials (SRMs) and other control materials, conduct of semi-annual interlaboratory comparison exercises, and the coordination of workshops to discuss the results of these exercises and to provide a forum for cooperative problem-solving efforts by participants. Since 1993, private sector and other laboratories that are not associated with these NOAA or EPA programs and that reimburse NIST for participation costs have participated in these exercises and workshops as part of the NIST Intercomparison Exercise Program for Organic Contaminants in the Marine Environment.

Current participants represent six multi-laboratory monitoring programs as well as a number of individual programs, and include eleven federal, six state/municipal, eleven university/college, eight private sector, and four international laboratories. In this performance-based program, each participating laboratory uses methods required by its program customers.

For the annual intercomparison exercises, a major activity of this QA program, samples of two natural-matrix-based homogeneous materials derived from the marine environment that have not been fortified with any of the target analytes are analyzed by the laboratories. Typical materials, such as mussel or fish tissue homogenates or wetted marine sediment, have target contaminant levels in the 1 to 600 μg/g range. At a workshop held in Miami, in December, 1993, the results of 1993 intercomparison exercises, Mussel V and Fish I, for 56 target analytes and percent moisture were presented and discussed. Numerical indices (z- and p-scores) are used to assess and track laboratory performance (for accuracy and precision) and provide a mechanism for assessing the comparability of data being produced by the participating laboratories. In general, the participating laboratories are meeting the accuracy and precision data quality criteria of their respective programs. Over half of the laboratories were participating in these exercises for the first time and typically did not perform as well as laboratories that had been participating for a number of years. In 1994, two intercomparison exercise materials, Mussel VI and Marine Sediment IV, were distributed to laboratories for analyses. Participants are performing concurrent analyses of appropriate specific reference materials and these results will be used in the exercise assessments as well. Exercise results for 1994, as well as analytical problems and solutions encountered during the year, will be discussed at the annual meeting to be held in January, 1995.

Several SRMs have been developed for this program including two natural matrix reference materials; (SRM 1941a, Organics in Marine Sediment, and SRM 1974a, Organics in Mussel Tissue) and six calibration solution SRMs. Five internal standard/surrogate solution reference materials requested by NOAA were produced this year and a sediment material with significantly higher levels of both organic and inorganic contaminants (relative to SRM 1941a) was collected and is being prepared as NIST SRM 1944.

Plans for next year include intercomparison exercises using two natural matrix materials and the annual workshop. Seven additional pesticides have been added to the list of evaluated analytes. In discussions with representatives of the European Community's similar QUASIMEME program (Quality Assurance of Information for Marine Environmental Monitoring in Europe), the use of common exercise material(s) that will provide a mechanism for assessment of comparability of results from participants in both programs is being investigated.

18. Quality Assurance Activities for the Measurement of Vitamins and Carotenoids in Human Serum and Food

J. Brown Thomas, D.L. Duewer, M.C. Kline, S.A. Margolis, and K.S. Sharpless

For the past ten years the National Institute of Standards and Technology has coordinated a Micronutrient Analysis Quality Assurance (QA) Program in conjunction with the National

Cancer Insitute (NCI), for laboratories that measure selected fat- and water-soluble vitamins, and carotenoids in serum and plasma. This program was initiated as part of investigations supported by the NCI Division of Cancer Prevention and Control to study the possible chemopreventive benefits of these micronutrients in populations of humans at high risk of contracting certain forms of cancer.

Two of the main components of the program have been (1) methods development and validation, and (2) interlaboratory quality assurance through use of proficiency testing. Serum-based samples with assigned values for the target analytes and performance-evaluation standards are distributed by NIST to approximately 65 domestic and foreign laboratories for analysis. NIST staff provide the laboratories with technical feedback concerning their performance and suggestions for methods development and refinement. The results from the proficiency testing are used to establish a laboratory performance database for use by NCI to evaluate the quality of the analytical data from which clinical conclusions are to be made.

In the past year the QA program consisted of three round robin exercises for the measurement of fat-soluble vitamins and carotenoids in serum, three studies for the measurement of ascorbic acid in serum, and one exercise for the measurement of fat-soluble vitamins and carotenoids in food. The core analytes in the program are: retinol, retinyl palmitate, α- and γ-tocopherol, and total β-carotene. Results are also summarized and evaluated for the following analytes: α-carotene, trans-β-carotene, β-cryptoxanthin, lutein, total lycopene, trans-lycopene, and zeaxanthin.

As a result of the QA program, the interlaboratory reproducibility of retinol, α-tocopherol, and β-carotene measurements has been maintained at the levels achieved shortly after the introduction of SRM 968, Fat-Soluble Vitamins in Human Serum, in 1989. For the past two years, the average estimated coefficient of variation for retinol and α-tocopherol has been approximately 10% and about 16% for β-carotene. Through the use of archived samples from previous round robin exercises, the longitudinal analysis stability of our participating laboratories' measurement capabilities has been demonstrated.

As part of the QA program, a workshop is held annually (or bi-annually in recent years) to allow participants the opportunity to discuss round robin results, analytical methods, and other related issues, and a one-day tutorial session is held annually, primarily for laboratories that are new to the QA program. As a result of our efforts to provide consultation services in methods development and refinement, the first methods manual, Methods for Analysis of Cancer Chemopreventive Agents in Human Serum, was completed in FY94 and will be available to all the participating laboratories in the coming year.

In the coming year the QA program structure will be similar to that of FY94 with an additional round robin exercise for the measurement of vitamins and carotenoids in food. Laboratories have expressed interest in improving the interlaboratory measurement capability for additional vitamins and carotenoids, such as β-cryptoxanthin, total lycopene, lutein, zeaxanthin, and retinyl palmitate. New program thrusts will include methods development for new analytes such as difluoromethylornithine and 4-hydroxyphenylretinamide. New agents that are currently in preclinical efficacy and toxicity testing (e.g., selenomethionine, epigallocatechin gallate, phenethyl isothiocyanate, indole-3-carbinol, dimethyl fumarate, and curcumin) will be incorporated into the program as they enter human clinical trials.

19. Development 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

Many damaging chemicals have been introduced into the marine environment during the last few decades. Organomercurials are among the most toxic of these contaminants due to their tendency to accumulate into biological tissues. Many analytical methods have been developed for the speciation of organomercury compounds in marine materials. However, most of these methods are time-consuming and inherently problematic. Furthermore, reference materials certified for methylmercury for a variety of sample types are desperately needed for quality assurance and method development in this field. At present there are no NIST reference materials with certified or NIST-assigned values for methylmercury. Several fish tissue reference materials certified for methylmercury are available from the National Research Council, Canada (NRCC), however, and certification of two human hair materials is in progress at the International Atomic Energy Association (IAEA, Vienna).

A new method has been developed for the extraction, speciation, and detection of methyl- and ethylmercury chloride in fish tissues, sediments, and human hair. Samples are extracted with organic solvent under acidic conditions to separate the analyte from the sample matrix. 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 high intensity of this mercury emission line permits both sensitive and selective detection of the analyte. The chromatographic separation and atomic emission detection were optimized for a variety of parameters.

The method was validated using the NRCC reference material DORM-1 (Dogfish Muscle), certified to contain 0.731 ± 0.060 mg/kg methylmercury as mercury in dried material. Analysis of five replicate DORM-1 samples using the new method results in a mean value of 0.780 ± 0.042 mg/kg methylmercury as mercury in dried material. Further validation of the new method using NRCC reference materials DOLT-2 (Dogfish Liver) and TORT-1 (Defatted Lobster) is in progress.

Several existing NIST marine tissue and sediment SRMs have been screened for methylmercury to determine their suitability for certification. Methylmercury is present in SRM 2704 (Buffalo River Sediment), SRM 2974 (Freeze-dried Mussel Tissue), SRM 1566a (Oyster Tissue), and SRM 1945 (Whale Blubber). Methylmercury was not detectable by this method in SRM 1588 (Cod Liver Oil) and SRM 1941a (Marine Sediment). Additional SRMs will be analyzed including SRM 1974a (Frozen Mussel Tissue) and SRM 1646 (Estuarine Sediment). After completion of these preliminary analyses, several of these materials will be selected for certification measurements in FY95.

20. On-Line Supercritical Fluid Extraction (SFE) - Gas Chromatography/Mass Spectrometry for the Analysis of Microgram Size Samples of Environmental and Forensic Interest

B.A. Benner, Jr. and J.F. Morrison

Soon after the mid-1980's, when citations describing analytical-scale supercritical fluid extraction (SFE) became more numerous in the analytical chemistry literature, descriptions of SFE directly interfaced with chromatographic methods [particularly gas chromatography (GC)] detailed the benefits of decompressing the supercritical fluid and the dissolved extract directly in the chromatographic column. One of the primary benefits of this on-line technique is that of increased sensitivity, as all of the organic extractable material from a solid sample is introduced into the analytical system, compared with only a few percent of the total from a conventional liquid solvent extract. Thus, the SFE-GC/mass spectrometric (MS) technique is practical for the extraction/analysis of samples in the microgram range and lower, depending on the concentrations of the desired analytes in the sample and the sensitivity of the detector.

In this last year, we have investigated the overall detection limit of on-line SFE-GC/MS using environmental Standard Reference Materials (SRMs) and air particulate samples collected in the field. We demonstrated the extraction and analysis of a number of hydrocarbon species (concentration in the hundreds of pg/μg) in a 37 μg sample of SRM 1650 (Diesel Particulate) using the MS detector in its full scan mode (50 - 550 amu). For a more sensitive and selective approach, we performed on-line SFE-GC/MS of a 48 μg sample of SRM 1649 (Urban Dust/Organics) with the MS detector monitoring for selected ions during the chromatographic run. This enabled detection of specific analytes (aromatic hydrocarbons) that are present in the SRM at 1 - 7 pg/μg. This same technique was also applied to 8 mm diameter circles taken from a filter blank and a filter used to collect suspended air particulate matter (particle aerodynamic diameters $\leq$ 10 μm) at a rural site, confirming the presence of aromatic hydrocarbons in the sample over any blank contributions. It should be noted that the size of the filter segment analyzed by SFE-GC/MS (0.50 cm^2) represented only 0.1% of the total filter area (20 x 25 cm = 500 cm^2) and an air volume of just 1.3 m^3.

The inherent increased sensitivity of this on-line extraction/analysis technique allows us to examine environmental samples of sizes ($\leq$ μg), which are not typically characterized for their chemical makeup, including size-segregated air samples, stratospheric particulate matter and ice core particulate matter. The method will also enable us to determine if several of NIST's natural matrix environmental SRMs are homogeneous at the μg sample size with respect to previously characterized organic species.

21. Quality Assurance for Health Care Measurements: Interactions with the College of American Pathologists

P. Ellerbe, S. Tai, L.T. Sniegoski, M.J. Welch and S. Long

The College of American Pathologists (CAP) is a large professional organization dedicated to furthering the science of pathology. CAP operates a large survey program for clinical laboratories to meet many governmental requirements for proficiency testing. It also provides a number of reference materials for clinical chemistry, enzymology, urine drug testing, and related fields. In the 1970's CAP and NIST recognized the critical need for accurate methods and reference materials to assess and improve the accuracy of routine clinical methods. In 1978, CAP began sponsoring a Research Associate (RA) to work full-time at NIST to develop highly accurate and precise (i.e., definitive) methods for clinical analytes. This program has continued throughout the intervening years and has grown to include three RAs, two in Division 835 and one in Division 834. Accurate methods and SRMs have been established for a number of important analytes, both organic and inorganic.

During FY94, the RAs completed development of a definitive method for serum triglycerides and applied it to analyses of several CAP survey materials. CAP initiated a large study of the applicability of fresh-frozen serum for use in surveys and as a reference material. Measurements of cholesterol were completed in FY94. The other analytes will be completed in FY95. Another area involves NIST and CAP reference materials for drugs of abuse in urine. In the past year, the RAs completed measurements of two CAP materials and one SRM, in addition to monitoring the stability of other materials. The third area involves verification and value assignment of CAP standard solutions used for calibration. During the past year these activities were aimed at cyanmethemoglobin and aqueous alcohol standard solutions.

The work in the Inorganic Analytical Research Division started this past year with the addition of a CAP-sponsored RA. His work has focussed on implementing definitive methods for important serum analytes and investigating if these methods could be transferred to the slightly less precise, but much faster ICP-MS technique. He has also investigating methods for trace element determinations in serum. During FY94 measurements were completed for several of the electrolytes in a number of CAP survey materials.

This program has demonstrated how government can work with the private sector to address important measurement problems. The progress here along with other technical developments have resulted in significant improvements in clinical laboratory accuracy. However, significant measurement challenges continue to increase, as new health-status markers, many of which are large molecules at very low concentration, continue to be found.

C. Outputs and Interactions
(Organic Analytical Research Division)

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Welch, M.J., Sniegoski, L.T., and Allgood, C.C., "Interlaboratory Comparison Studies on the Analysis of Hair for Drugs of Abuse," Forensic Sci. Inter'l. 63, 295-303 (1993).

Welch, M.J., Ellerbe, P., Tai, S.S.-C., Christensen, R.G., Sniegoski, L.T., Sander, L. C., and Phinney, C.S., "NIST Reference Materials to Support Accuracy in Drug Testing," Fresenius' J. Anal. Chem. (in press).

Welch, M.J. and Sniegoski, L.T., "Interlaboratory Studies on the Analysis of Hair for Drugs of Abuse - Results from Three Exercises," NIDA Special Publication (in press).

Wise, S.A., Koster, B.J., Langland, J.L., and Zeisler, R., "Current Activities within the National Biomonitoring Specimen Bank," Sci. Total Environ. 139/140, 1-12 (1993).

Wise, S.A., "Standard Reference Materials for the Determination of Trace Organic Constituents in Environmental Samples," Environmental Analysis--Techniques, Applications and Quality Assurance, D. Barcelo, Elsevier Science Publishers, Amsterdam, The Netherlands, 403-446 (1993).

Wise, S.A. and Koster, B.J., "Considerations in the Design of an Environmental Specimen Bank: Experiences of the National Biomonitoring Specimen Bank Program," Environ. Health Perspect. (in press).

Zeisler, R., Demiralp, R., Koster, B.J., Becker, P.R., Burow, M., Ostapczuk, P. and Wise, S.A., "Determination of Inorganic Constituents in Marine Mammal Tissues," Sci. Total Environ. 139/140, 365-386 (1993).

2. Talks

Behlke, M., "Organomercury Speciation in Marine Reference Materials by Gas Chromatography with Atomic Emission Detection," University of Massachusetts, Amherst, MA, October 19, 1993.

Behlke, M., "Organomercury Speciation in Marine Standard Reference Materials by Gas Chromatography with Atomic Emission Detection," Pittsburgh Conference, Chicago, IL, March 1, 1994.

Benner, Jr., B., "Supercritical Fluid Extraction of Natural Matrix Standard Reference Materials," NIST Workshop on Supercritical Fluid Extraction: Technology of the Future, Boulder, CO, November 30, 1993.

Benner, Jr., B., "Supercritical Fluid Extraction of Natural Matrix Standard Reference Materials", 5th International Symposium on Supercritical Fluid Chromatography and Extraction, Baltimore, MD, January 11, 1994. Invited

Benner, Jr., B., "Supercritical Fluid Extraction of Environmental Samples," Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, April 15, 1994. Invited

Brown Thomas, J., "The Determination of Fat- and Water-Soluble Vitamins in SRM 1846, Infant Formula," 208th American Chemical Society National Meeting, Washington, DC, August 21, 1994.

Bunk, D.M., "Characterization of Pyoverdine Pf244 Fragmentation Using ESI-MS/MS," 42nd ASMS Conference on Mass Spectrometry and Allied Topics, Chicago, IL, May 30, 1994.

Bunk, D.M., "Quantitative Electrospray Ionization Mass Spectrometry of Proteins," 42nd ASMS Conference on Mass Spectrometry and Allied Topics, Chicago, IL, June 2, 1994.

Bunk, D.M., "Quantitative Protein Analysis Using Electrospray Ionization Mass Spectrometry," 13th International Mass Spectrometry Conference, Budapest, Hungary, August 29, 1994.

Choquette, S., "Integrated Optic Interferometry for Thermal Immunoassay in Flow Injection Analysis," XXth Federation of Analytical Chemists and Spectroscopists Societies (FACSS), Detroit, MI, October 5, 1993.

Choquette, S., "Integrated Optic Radiation Dosimeters," Photonic Sensor Systems Expo '93, Philadelphia, PA, October 27, 1993.

Choquette, S., "Integrated Optical Chemical Sensors," 2nd Workshop on Integrated Optics for Military and Commercial Applications," Huntsville, AL, December 7, 1993. Invited

Choquette, S., "Review of Optical Waveguides Sensors for Bio/Chemical and Environmental Applications, Photonic Sensor Systems Expo '94, Cleveland, OH, September 20, 1994.

Choquette, S., "Automated Immunoassays Using Flow and Planar Optical Waveguide Detectors," Army Research Laboratory, Aberdeen Proving Ground, MD, June 9, 1994. Invited

Choquette, S., "Future Directions in Optical Biosensor Development," Institute of Food Technologists Annual Meeting, Atlanta, GA, June 27, 1994. Invited

Dorko, W.D., "Calibration Gas Standard Reference Materials," Department of Science Services, Bankok, Thailand, January 19, 1994. Invited

Dorko, W.D., "Primary Gas Standards and Their Use in Reference Materials Programs," Department of Science Services, Bankok, Thailand, January 26, 1994. Invited

Dorko, W.D., "Gas Dynamic Dilution Systems for Instrument Calibration," Dynamic Dilution Workshop, NIST, Gaithersburg, MD, February 22, 1994.

Dorko, W.D., "The NIST Traceable Reference Material Gas Mixture Program," Gas Standards Workshop, Chicago, IL, February 27, 1994.

Dorko, W.D., "Uncertainties in the NIST Atmospheric Carbon Dioxide Standard Reference Materials," National Oceanic Atmospheric Administration/Climate Monitoring & Diagnostic Laboratory Meeting, Boulder, CO, March 9, 1994. Invited

Dorko, W.D., "Implementation of the NIST Traceable Reference Program by Specialty Gas Companies," Linde de Mexico, Mexico City, Mexico, August 23, 1994. Invited

Dorko, W.D., "Preparation and Verification of Primary Gas Standards," CENAM, Querataro, Mexico, August 26, 1994. Invited

Gray, M., "A Sensitive Microenzymatic Fluorescence Assay for Serum Cholesterol," National Organization for the Professional Advancement of Black Chemists and Chemical Engineers, Atlantic City, NJ, April 6, 1994.

Gray, M., "Microenzymatic Assay for Serum Cholesterol Determination," American Association for Clinical Chemistry, Tampa, FL, April 15, 1994.

Gray, M., "Immunospecific Enzymatic Assay for Serum Lipoprotein Cholesterol Determination," 208th American Chemical Society Middle Atlantic Regional Meeting, Baltimore, MD, May 25, 1994.

Guenther, F.R., "The NIST Gas Metrology Research Program," Gas Standards Workshop, Chicago, IL, February 27, 1994.

Guenther, F.R., "NIST Volatile Organic Compound Standards," Sixth International Symposium on Biological and Environmental Reference Materials (BERM-6), Kailua-Kona, Hawaii, April 20, 1994.

Guenther, F.R., "Defining Traceability: The NIST Traceable Reference Material Program," Sixth International Symposium on Biological and Environmental Reference Materials (BERM-6), Kailua-Kona, Hawaii, April 20, 1994.

Hillery, B., "Enhancement of Selectivity for Planar Compounds in Supercritical Fluid Chromatography," 5th International Symposium on Supercritical Fluid Chromatography and Extraction, Baltimore, MD, January 11, 1994.

Hillery, B., "Characterization of Polychlorinated Biphenyl Technical Mixtures on a Novel Cyanobiphenyl Stationary Phase," 208th American Chemical Society National Meeting, Washington, DC, August 21, 1994.

Hillery, B., "Comparison of Selectivities for a Series of Cyanobiphenyl Stationary Phases," 16th International Symposium on Capillary Chromatography, Riva del Garda, Italy, September 27, 1994.

Hillery, B., "Quantitative Analysis of Selected PCB Congeners in Marine Matrix Reference Materials, 16th International Symposium on Capillary Chromatography, Riva del Garda, Italy, September 27, 1994.

Kramer, G., "The NIST Consortium on Automated Analytical Laboratory Systems (CAALS)," 34th ORNL-DoE Conference on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 5, 1993. Invited

Kramer, G., "CAALS-I Communication Specification" Scientific Computing and Automation Meeting, Crystal City, VA, October 13, 1993. Invited

Kramer, G., "Presentation of the Pioneer in Laboratory Robotics Awards," International Symposium on Laboratory Robotics and Automation Meeting, Boston, MA, October 18, 1993. Invited

Kramer, G., "Standards for Automated Analytical Laboratory Instruments: Where Are We? Where Do We Want To Go? How Can We Get There From Here?," 14th Annual Analytical Laboratory Managers Association Meeting, Louisville, KY, October 21, 1993. Invited

Kramer, G., "Laboratory Robotics in Today's Laboratory" 3rd International Symposium on Laboratory Robotics and Artificial Intelligence Applied to Analytical Chemistry and Laboratory Medicine, San Diego, CA, January 25, 1994.

Kramer, G., "The NIST Consortium on Automated Analytical Laboratory Systems," Consortium on Advanced Biosensors Meeting, Gaithersburg, MD, February 24, 1994. Invited

Kramer, G., "The NIST Consortium on Automated Analytical Laboratory Systems (CAALS)-Standards for Automated Systems Used in Analytical Chemistry," Pittsburgh Conference, Chicago, IL, March 3, 1994.

Kramer, G., "The Evolution of the Consortium on Automated Analytical Laboratory Systems," 8th International Laboratory Information Management (LIMS) Conference,Pittsburgh, PA, June 7, 1994. Invited

Kramer, G., "Sociology for System Devices: Standards for the Behavior of Instruments in Automated Systems," Colloque d'Automatisation et Robitisation des Operations dans les Laboratoires de Chemie et de Biochemie at the Conservatoire National des Arts et Metiers, Paris, France, June 17, 1994. Invited

Kramer, G., "NIST Activities Related to Healthcare and the Clinical Laboratory," Clinical Testing Automation Standards Steering Committee (CTASSC), New Orleans, LA, July 19, 1994. Invited

Kramer, G., "Etiquette for Automated Devices," 108th Association of Official Analytical Chemists Annual International Meeting, Portland, OR, September 13, 1994. Invited

Leister, D., "Observed Distribution Coefficients of Organic Contaminants in Rain -- Implications of Particles in the Removal of Organic Contaminants from the Atmosphere via Precipitation," American Geophysical Union National Meeting, Baltimore, MD, May 26, 1994. Invited

Leister, D., "A Novel Method for Measuring the Submicron Particle-Size Distribution of PAHs in the Atmosphere," 37th Conference on Great Lakes Research, International Associate for Great Lakes Research '94 Estuarine Research Meeting, Windsor, Ontario, Canada, June 6-9, 1994. Invited

Leister, D., "Methods Employed to Measure Organic Contaminants in Precipitation in the Chesapeake Bay Region," Environment Canada, Waterloo, Ontario, Canada, June 16-18, 1994. Invited

Leister, D., "High Volume Water Sampling Using XAD-2 Macroreticular Resin: Methodology and Field Applications," Environment Canada, Waterloo, Ontario, Canada, June 16-18, 1994. Invited

Locascio-Brown, L., "Simultaneous Measurement of Estrogen Hormone Metabolites Using Flow Injection Immunoassay for Assessment of Cancer," XXth Federation of Analytical Chemists and Spectroscopists Societies (FACSS), Detroit, MI, October 5, 1993. Invited

Locascio-Brown, L., "Novel Immunoassay Based Technology for Assessing Breast Cancer Risks," National Organization for the Professional Advancement of Black Chemists and Chemical Engineers, Atlantic City, NJ, April 6, 1994. Invited

Locascio-Brown, L., "Novel Immunoassays for Measurement of Hormone Metabolites to Assess Cancer Risk," 1994 Society for Applied Spectroscopy Speaker Tour, Indianapolis, IN, April 20, 1994. Invited

Locascio-Brown, L., "Novel Immunoassays for Measurement of Hormone Metabolites to Assess Cancer Risk," 1994 Society for Applied Spectroscopy Speaker Tour, Vancouver, British Columbia, Canada, April 21, 1994. Invited

Locascio-Brown, L., "Novel Immunoassays for Measurement of Hormone Metabolites to Assess Cancer Risk," 1994 Society for Applied Spectroscopy Speaker Tour, Gregson, MT, June 25, 1994. Invited

MacCrehan, W., "Supercritical Fluid Extraction of Environmental Samples Using Carbon Dioxide and Fluoroform," NIST Workshop on Supercritical Fluid Extraction: Technology of the Future, Boulder, CO, November 30, 1993.

MacCrehan, W., "Temporal Variation of Organic and Inorganic Sulfur in an Anoxic Chesapeake Bay Sediment," 208th American Chemical Society National Meeting, Washington, DC, August 22, 1994.

Margolis, S., "Ascorbic Acid Assay - A Collaborative Assessment of Laboratory Accuracy and Precision," Federation of American Societies for Experimental Biology, American Institute of Nutrition, Anaheim, CA, April 26, 1994.

May, W.E., "NIST Research Programs in Organic Analytical Chemistry," Morgan State University, Chemistry Department, January 25, 1994. Invited

May, W.E., "NIST Research, Measurement Services, and Quality Assurance Activities in Support of NCI Cancer Chemoprevention Studies," First International Symposium on the Role of Soy in Preventing and Treating Chronic Disease, Mesa, AZ, February 20, 1994. Invited

May, W.E., "Organic Analytical Research Activities at the National Institute of Standards and Technology", Chemistry Department, Villanova University, Villanova, PA, March 22, 1994. Invited

May, W.E., "NIST Research and Measurement Activities in Support of the AIGER CRADA", Society of Automotive Engineers Meeting, Washington, DC, March 29, 1994. Invited

May, W.E., "NIST Measurement Capabilities: Modes for Interaction", 1994 Analytical and Testing Conference, Holiday Inn Convention Center, Midland, MI, May 25, 1994. Invited

May, W.E., "NIST Research and New Technology Development in Support of AIGER", AIGER Office, General Motors Research Center, Detroit, MI, May 26, 1994. Invited

May, W.E., "Opportunities for NIST and the Mayo Clinic in the Area of Health Care Technology", Mayo Clinic, Rochester, MN, June 30, 1994. Invited

May, W.E., "Career Opportunities in the Chemical Sciences: The Need for More African American Involvement", Bowie State University Summer Emerging Scholars Program, Bowie, MD, July 27, 1994. Invited

Mitchell, G.D., "The Use of Reference Materials in Organic Analytical Chemistry Measurements," NIST Workshop on the Use of Standard Reference Materials for Quality Assurance, Harare, Zimbawe, July 27, 1994. Invited

Morrison, J., "The Use of CO_2-Modified Fluids for the Selective Recovery of Polar Drugs of Abuse from Hair," NIST Workshop on Supercritical Fluid Extraction: Technology of the Future, Boulder, CO, November 30, 1993.

Morrison, J., "Supercritical Fluid Extraction of Cocaine from Human Hair Using CO_2 Modified with Water and Triethylamine," 5th International Symposium on Supercritical Fluid Chromatography and Supercritical Fluid Extraction, Baltimore, MD, January 11, 1994.

Morrison, J., "Extraction of Drugs of Abuse from Human Hair Using Supercritical Fluids," First Annual Sigma Xi Post-Doctoral Poster Presentation, NIST, Gaithersburg, MD, February 24, 1994.

Morrison, J., "Evaluation of Supercritical Fluid Extraction for the Selective Recovery of Drugs-of-Abuse from Hair," 2nd International Meeting on Clinical and Forensic Aspects of Hair Analysis, Genoa, Italy, June 7, 1994. Invited

Morrison, J., "Supercritical Fluid Extraction of Drugs of Abuse from Hair," Bureau of Alcohol, Tobacco, and Firearms National Laboratory Center, Rockville, MD, June 29, 1994. Invited

Page, S., "Evaluation of Phase Behavior on Supercritical Fluid Extraction Performance," NIST Workshop on Supercritical Fluid Extraction: Technology of the Future, Boulder, CO, November 30, 1993.

Page, S., "Restrictor Plugging in High Temperature Off-Line Supercritical Fluid Extraction of Environment Samples: Microscopic and Spectroscopic Analyses", 5th International Symposium on Supercritical Fluid Chromatography and Extraction, Baltimore, MD, January 11, 1994.

Page, S., "Measurement and Influence of Phase Behavior on Supercritical Fluid Chromatography and Extraction," 5th International Symposium on Supercritical Fluid Chromatography and Extraction, Baltimore, MD, January 11, 1994.

Parris, R., "NIST Standard Reference Materials for Organic Environmental Analyses," Eastern Analytical Symposium, Somerset, NJ, November 15, 1993. Invited

Parris, R., "The NIST Intercomparison Exercise Program for Organic Contaminants in the Marine Environment - Components of a Performance-Based Quality Assurance Program," Eastern Analytical Symposium, Somerset, NJ, November 15, 1993.

Parris, R., "Results of NIST/NOAA NS&T/EPA EMAP FY93 Intercomparison Exercises for Organic Contaminants in the Marine Environment," 1993 National Oceanic and Atmospheric Administration Meeting, Miami, FL, December 7-8, 1993.

Parris, R., "Mechanisms for Measurement Comparability Assessment," Workshop on NHEXAS Analytical Measurement Comparability Assessment, EPA, Research Triangle Park, NC, January 11, 1994.

Parris, R., "A Review of Recent NIST Standard Reference Materials for the Marine Environment," ICES Meeting, Brest, France, February 7-12, 1994.

Parris, R., "A Review of the NIST Intercomparison Exercise Program for Organic Contaminant in the Marine Environment," ICES Meeting, Brest, France, February 7-12, 1994.

Parris, R., "Organics in the Marine Environment: Mechanisms for Measurement Comparability Assessment," 37th Conference on Great Lakes Research, International Associate for Great Lakes Research '94 Estuarine Research Meeting, Windsor, Ontario, Canada, June 9, 1994. Invited

Parris, R., "Getting a Measurement Process Under Control - A Case Study," 208th American Chemical Society National Meeting, Washington, DC, August 24, 1994. Invited

Phinney, C.S., "Determination of 11-nor-delta-9-tetrahydrocannabinol-9-carboxylic Acid by Tandem-in-Time Ion Trap Mass Spectrometry," 42nd ASMS Conference on Mass Spectrometry and Allied Topics, Chicago, IL, May 31, 1994.

Sams, R.L., "Line Strengths of Some Selected Transitions in the 2900 CM^1 Region of H_2CO," Optical Sensing for Environmental Monitoring Meeting, Atlanta, GA, October 11, 1993.

Schantz, M., "Gas Chromatographic Methods for the Determination of PCB Congeners and Chlorinated Pesticides in Marine Reference Materials," XXth Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Detroit, MI, October 19, 1993.

Schantz, M., "Use of Perdeuterated and Carbon-13 Labeled Polycyclic Aromatic (PAHs) as Internal Standards for the Determination of PAHs in Natural Matrix Standard Reference Materials (SRMs), 207th American Chemical Society National Meeting, San Diego, CA, March 15, 1994.

Schantz, M., "NIST Analytical Method for Analyses of Marine Mammal Tissues," ECD/NIST Quality Assurance Meeting, Seattle, WA, July 21, 1994.

Schantz, M., "Standard Reference Materials for the Determination of Polycyclic Aromatic Hydrocarbons in Environmental Samples," 208th American Chemical Society National Meeting, Washington, DC, August 25, 1994.

Schantz, M., "Update on NIST Activities," NHEXAS Planning Meeting, Research Triangle Park, NC, September 17, 1994.

Sharpless, K., "Development of Reference Materials for Vitamins and Carotenoids in Food," 208th American Chemical Society National Meeting, Washington, DC, August 21, 1994.

Siles, B., "The Synthesis and Characterization of Homopolypeptide Bonded Stationary Phases for Liquid Chromatography," 1st Annual Sigma-Xi Post-Doctoral Poster Presentation, NIST, Gaithersburg, MD February 24, 1994.

Sniegoski, L.T., "Interlaboratory Studies on the Analysis of Drugs of Abuse in Hair," 2nd. International Meeting on Clinical and Forensic Aspects of Hair Analysis, Genova, Italy, June 6, 1994. Invited

Welch, M.J., "Activities at the National Institute of Standards and Technology to Support Accuracy in Drugs of Abuse Testing," Tactical Technologies and Wide Area Surveillance International Symposium, Chicago, IL, November 2, 1993.

Welch, M.J., "Development of NIST Traceable Reference Materials (NTRMs)," Quality Management Systems for Environmental Monitoring and Measurements Workshop, Cairo, Egypt, March 23, 1994. Invited

Welch, M.J., "Development and Certification of Environmental Reference Materials - A Case Study," Quality Management Systems for Environmental Monitoring and Measurements Workshop, Cairo, Egypt, March 23, 1994. Invited

Welch, M.J., "Survey of Analytical Environmental Measurement Techniques," Quality Management Systems for Environmental Monitoring and Measurements Workshop, Cairo, Egypt, March 23, 1994. Invited

Welch, M.J., "Certification of SRM 1511, Multi-Drugs of Abuse in Freeze-Dried Urine," Sixth International Symposium on Biological and Environmental Reference Materials (BERM-6), Kailua-Kona, Hawaii, April 18, 1994.

Welch, M.J., "NIST Programs to Support Accuracy in Drug Testing," NIDA Technical Review: The Validity of Self-Reported Drug Use, Gaithersburg, MD, September 8, 1994.

Welch, M.J., "Development of Stable Isotope Dilution Mass Spectrometry Methodology to Characterize SRM 1544 Fatty Acids in Diet Composite," Association of Official Analytical Chemists Annual Meeting, Portland, OR, September 12, 1994.

Wise, S., "Chromatographic Approaches to the Determination of Polycyclic Aromatic Hydrocarbons in Environmental Reference Materials," XXth Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), Detroit, MI, October 19, 1993.

Wise, S., "Chromatographic Measurements of Contaminants in Environmental Samples," Department of Chemistry, Illinois Institute of Technology, Chicago, IL, November 3, 1993. Invited

Wise, S., "Chromatographic Approaches to the Measurement of Organic Contaminants in Environmental Samples," Department of Chemistry, Howard University, Washington, DC, November 12, 1993. Invited

Wise, S., "The Measurement of Organic Pollutants in Environmental Samples," Department of Chemistry and Biochemistry, Southern Illinois University at Carbondale, Carbondale, IL, December 3, 1993. Invited

Wise, S., "Chromatographic Approaches to the Measurement of Organic Contaminants in Environmental Samples," Department of Chemistry, University of Massachusetts at Amherst, December 13, 1993. Invited

Wise, S., "Status of Standard Reference Materials for the Marine Environment," Annual NOAA Workshop on Quality Assurance for the NS&T Program, Miami, FL, December 9, 1993. Invited

Wise, S., "Preparation and Certification of Environmental Standard Reference Materials," Department of Science Service, Bangkok, Thailand, February 10, 1994. Invited

Wise, S., "Development of Reference Materials for Vitamins and Carotenoids in Food Matrices," 6th International Symposium on Biological and Environmental Reference Materials (BERM-6), Kona, HI, April 18, 1994.

Wise, S., "Certification Approach for the Determination of PCB Congeners and Chlorinated Pesticides in Marine Reference Materials," 6th International Symposium on Biological and Environmental Reference Materials (BERM-6), Kona, HI, April 20, 1994.

Wise, S., "Certification and Reissue of Marine Sediment (SRM 1941a) and Mussel Tissue (SRM 1974a) Reference Materials for the Determination of Organic Contaminants," 6th International Symposium on Biological and Environmental Reference Materials (BERM-6), Kona, HI, April 20, 1994.

Wise, S., "Certification of SRM 1945, Organics in Whale Blubber," 6th International Symposium on Biological and Environmental Reference Materials (BERM-6), Kona, HI, April 20, 1994.

Wise, S., "Chromatographic Approaches to the Determination of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls in Environmental Standard Reference Materials," Deauville Conference 94 (13th International Symposium on Microchemical Techniques and 2nd International Symposium on Analytical Sciences), Montreux, Switzerland, May 16, 1994. Invited

Wise, S., "Problem Solving at NIST -- The Making of a Standard Reference Material," Symposium on Problem Solving in the 90's, North Jersey Chromatography Topical Group, AT&T Bell Laboratories, Murray Hill, NJ, June 9, 1994. Invited

3. Cooperative Research Development Agreements (CRADAs) and Consortia

Bio/Chemical Reagent Immobilization on Integrated Optic Hartman Interferometers for Immunosensing, S. Choquette and L. Locascio-Brown
Photonic Sensor Systems (CRADA)

Clinical Laboratory Work, M.J. Welch
  College of American Pathologists (CRADA)

Consortium on Automated Analytical Laboratory Systems, G. Kramer
  Abbott Laboratories (CRADA)
  Boehringer Mannheim Corporation (CRADA)
  BP America (CRADA)
  Digital Equipment Corporation (CRADA)
  E.I. Dupont de Nemours Company (CRADA)
  Eastman Chemical Company (CRADA)
  Eastman Kodak Company (CRADA)
  Hewlett Packard Company (CRADA)
  The Perkin Elmer Corporation (CRADA)

Ethanol Gas Standards, F.R. Guenther
  Scott Specialty Gases (CRADA)

Preparation of a Quality Assurance Standard, R.G. Christensen
  Union Carbide Corporation (CRADA)

4. Patent Awards and Applications

Plant, A.L., Locascio-Brown, L., and Durst, R.A., "Liposome-Enhanced Flow Injection Immunoanalysis" (allowed July 1994)

5. SRM Activities

SRM 909b	Human Serum
SRM 968b	Fat-Soluble Vitamin in Human Serum
SRM 1507b	Marijuana Metabolite in Freeze-Dried Urine
SRM 1511	Multi-Drugs of Abuse in Freeze-Dried Urine
SRM 1544	Fatty Acids in a Food Composite
SRM 1563	Coconut Oil
SRM 1613a	20 ppm CO in Air
SRM 1614a	42 ppm CO in Air
SRM 1649a	Urban Dust/Organics
SRM 1660a	4 ppm CH_4, 1 ppm Propane in Air
SRM 1671a	345 ppm CO_2 in Air
SRM 1672a	355 ppm CO_2 in Air
SRM 1676a	362 ppm CO_2 in Air
SRM 1677c	9.6 ppm CO in Nitrogen
SRM 1678c	50 ppm CO in Nitrogen
SRM 1680b	500 ppm CO in Nitrogen
SRM 1681b	1000 ppm CO in Nitrogen

SRM 1683b	50 ppm NO in Nitrogen
SRM 1684b	100 ppm NO in Nitrogen
SRM 1685b	245 ppm NO in Nitrogen
SRM 1686b	500 ppm NO in Nitrogen
SRM 1687b	1000 ppm NO in Nitrogen
SRM 1693a	50 ppm SO_2 in Nitrogen
SRM 1694a	100 ppm SO_2 in Nitrogen
SRM 1800	5 ppb NMOC
SRM 1845	Whole Egg Powder
SRM 1846	Infant Formula
SRM 1941a	Organics in Marine Sediment
SRM 1945	Organics in Whale Blubber
SRM 1974a	Organics in Mussel Tissue (*Mytilus edulis*)
SRM 1975	Diesel Particulate Extract
SRM 2286	2.0% Ethanol in Gasoline
SRM 2287	3.5% Ethanol in Gasoline
SRM 2288	2.0% TAME in Gasoline
SRM 2289	2.7% TAME in Gasoline
SRM 2290	2.0% ETBE in Gasoline
SRM 2291	2.7% ETBE in Gasoline
SRM 2292	2.0% MTBE in Gasoline
SRM 2293	2.70% MTBE in Gasoline
SRM 2383	Carotenoids and Fat-Soluble Vitamins in Food
SRM 2622a	1.96 % CO_2 in Nitrogen
SRM 2626a	3.92 % CO_2 in Nitrogen
SRM 2627a	5 ppm NO in Nitrogen
SRM 2628a	10 ppm NO in Nitrogen
SRM 2630	1500 ppm NO in Nitrogen
SRM 2642/a	7.8% CO in Nitrogen
SRM 2658a	9.7% Oxygen in Air
SRM 2659a	21% Oxygen in Air
SRM 2660	100 ppm NO_x in Air
SRM 2730	5 ppm H_2S in Nitrogen
SRM 2731	20 ppm H_2S in Nitrogen
SRM 2764	0.25 ppm Propane in Air
SRM 2974	Organics in Mussel Tissue (Freeze Dried)
RM 8509	Moisture in Methanol (100 μg/g)
RM 8510	Moisture in Methanol (400 μg/g)
RM 8532	Diesel Fuel 0.1
RM 8045	Mussel Tissue (GESREM II)

6. SRD Activities

None

7. Calibrations

(gas cylinder recertifications)

Air Liquid [3]
Airco Specialty Gases [26]
Airgas [7]
Air Products [12]
Department of Navy, Western Standards Lab [8]
Desert Research Institute - 1
Florida Dept. of Environmental Regulations [2]
Fraunhofer Institut fur Atmospharische Umweltforschung [1]
Honda of North America [1]
Liquid Air, Alphagaz [6]
Liquid Carbonic [4]
MG Industries [1]
NABEL/EMPA - Germany [1]
National Center for Atmospheric Research [1]
Scott Marin, Inc. [1]
Scott Specialty Gases [7]
State of Connecticut - EPA [1]
State of New Mexico [1]
State of Wisconsin - Department of Natural Resources [1]
Tennessee Valley Authority [1]
U.S. EPA [7]
University of Stockholm [1]
Westinghouse Hanford Company [1]

8. Committee Assignments

J. Brown Thomas

SCW Education Committee - Chair

W.D. Dorko

ASTM D2203 Ambient Atmospheres and Source Emissions
ASTM D2205 Indoor Air
Advisory Committee of Gaseous Sulfur Analysis Intercomparison Experiment
Chemical Society of Washington, Meeting Arrangements Committee

G.W. Kramer

ASTM, E31 Computerized Systems
ASTM, SC E31.40 Laboratory Information Management Systems
ASTM, E49 Computerization of Material Property Data
ASTM, SC E49.52 Experimental Data Interchange
Clinical Testing Automation Standards Steering Committee (CTASSC)

W.E. May

American Chemical Society, Presidents Blue Ribbon Panel on Minority Affairs
International Society for Polycyclic Aromatic Compounds, President
Physical Science Panel, Ford Foundation Predoctoral Fellowship Evaluation Board, Chair
Federal Interagency Coordinating Committee for National Human Exposure Assessment Survey (NHEXAS)
U.S. Government Interdepartmental Minority Health/Science Careers Coordinating Committee
Rapporteur for Chemical Metrology, NORAMET

R.M. Parris

Washington Chromatography Discussion Group (Secretary)

M.M. Schantz

Washington Chromatography Discussion Group (President)

M.J. Welch

Standards Committee of the College of American Pathologists (Advisor)
NCCLS Sub-Committee on Cholesterol in Serum Reference Materials

E. White V

EPA Toxic Substances Control Act Interagency Testing Committee, DoC Representative

S.A. Wise

American Chemical Society, Division of Analytical Chemistry, Publicity Committee, Chair
International Society for Polycyclic Aromatic Compounds (ISPAC), Program Committee, Co-chair

9. Editorships

G.W. Kramer

Laboratory Robotics and Automation (Editorial Advisory Board)
American Chemical Society, Computer Buyer's Guide
Laboratory Automation Standards Foundation (LA Forum Standards Issues Editor)

S.A. Wise

Fresenius' Journal of Analytical Chemistry (Editorial Advisory Board)
Journal of Microcolumn Separations (Editorial Advisory Board)

10. Seminars

November 1, 1993

Dr. Nicholas Fell, Jr., Department of Chemistry and Beckman Institute, University of Illinois and Urbana-Champaign, Urbana, IL, "Characterization of Diffusion Processes in Thin Polymer Films Via Optical Waveguide Techniques." (Division Sponsor: S.J. Choquette)

November 4, 1993

Dr. Jiri Janata, Molecular Science Research Center, Pacific Northwest Laboratories, Richland, WA, "Environmental Sensing at Hanford." (Division Sponsor: L. Locascio-Brown)

November 15, 1993

Mr. Cy Pollema, Department of Chemistry, University of Washington, Seattle, WA, "A Study of Reaction Surfaces for Use in Flow Injection Immunoanalysis." (Division Sponsor: L. Locascio-Brown)

November 19, 1993

Dr. Steven Hawthorne, Energy and Environmental Research Center, University of North Dakota, Grand Forks, ND, "Validating Supercritical Fluid Extraction (SFE) Methods Using SRMs (Just What is "Quantitative," Anyway?)." (Division Sponsor: S.A. Wise)

December 16, 1993

Dr. Ronald Lee, Surface Science Group, Naval Surface Warfare Center, Silver Spring, MD, "Structure of Process Information: Analytical Data and Manufacturing." (Division Sponsor: G.W. Kramer)

February 18, 1994

Dr. Thomas Chester, Miami Valley Laboratories, Procter and Gamble Co., Cincinnati, OH, "Industrial Perspective of Supercritical Fluid Chromatography." (Division Sponsor: M.M. Schantz)

February 24, 1994

Mr. Anthony Lemmo, Department of Chemistry, University of North Carolina, Chapel Hill, NC, "Comprehensive Two-Dimensional Separation of Protein Mixtures by Microcolumn LC-CZE." (Division Sponsor: S.A. Wise)

March 7, 1994

Ms. Nicole Schultz, Department of Chemistry, University of Florida, Gainesville, FL, "Rapid Immunoassay by Capillary Zone Electrophoresis with Detection Fluorescence." (Division Sponsor: S.A. Wise)

March 10, 1994

Dr. Donald Dahlberg, Department of Chemistry, Lebanon Valley College of Pennsylvania, Annville, PA, "Standardization of Chromatograms." (Division Sponsor: D.L. Duewer)

March 28, 1994

Mr. Tom Cambron, Department of Chemistry, University of Utah, Salt Lake City, UT, "Development of Time-Resolved Laser Calorimetry Methods for Monitoring Photoinitiated Free-Radical Reactions." (Division Sponsor: S.A. Wise)

April 7, 1994

Dr. Brigitte Ramos, Department of Chemistry, University of Cincinnati, Cincinnati, OH, "Polymer Modified Micro Electrodes as Sensors for Radiopharmaceutical Analogs." (Division Sponsor: S.J. Choquette)

June 9, 1994

Dr. Anne M. Andrews, NIST, Gaithersburg, MD, "Subtlety in Infrared Spectroscopy at High Resolution," (Division Sponsor: F. R. Guenther)

June 16, 1994

Dr. David M. Bunk, NIST, Gaithersburg, MD, "Electrospray Ionization Mass Spectrometry of Proteins Theory and Application." (Division Sponsor: M. J. Welch)

July 6, 1994

Mr. Robert Clark, Tripos Associates, Inc., St. Louis, MO, "An Industrial Organic Chemist's View of Computational Chemistry." (Division Sponsor: D.L. Duewer)

July 25, 1994

Dr. Mark Russo, Sterling Winthrop, Malvern, PA, "FlexBench: Flexible Automation for Cost-Effective Laboratory Research." (Division Sponsor: G.W. Kramer)

August 31, 1994

Dr. Carl Selavka, National Medical Services, Inc., Willow Grove, PA, "Big Hairy Deal: The Forensic World of Hair Drug Testing." (Division Sponsor: J.F. Morrison)

September 20, 1994

Dr. Roger van Zee, NIST, Gaithersburg, MD, "The Dynamics of the Reaction $O(^1D)+CH_4 \rightarrow OH+CH_3$ Initiated in $CH_4 \bullet O_3$ Clusters." (Division Sponsor: F. R. Guenther)

September 29, 1994

Dr. Kevin L. McNesby, Army Research Lab, Aberdeen, MD, "Corrections to Line-of-Sight Tunable Diode Laser Spectra of Low Pressure Flames." (Division Sponsor: F. R. Guenther)

September 30, 1994

Dr. Joel Baker, Center for Environmental and Estuarine Studies, Chesapeake Biological Laboratory, University of Maryland, Solomons, MD, "Accumulation of Persistent Organic Contaminants in Aquatic Food Webs: Was W.C. Fields Correct?" (Division Sponsor: D.L. Leister)

11. Conferences/Workshops/Sessions Sponsored/Co-Sponsored

September 24, 1993

Fat-Soluble Vitamin and Carotenoid Analysis Tutorial, NIST, Gaithersburg, MD (J. Brown Thomas)

November 9-10, 1993

CAALS Oversight Board Meeting, Hewlett Packard, Wilmington, DE (G. Kramer)

January 11-12, 1994

NHEXAS Analytical Measurement Methods and QA Workshop, Research Triangle Park, NC (W.E. May)

February 22, 1994

Gas Dynamic Dilution Meeting, NIST, Gaithersburg, MD (W.D. Dorko)

February 27, 1994

Calibration Gas Standards Workshop, Chicago, IL (W.E. May, F.R. Guenther and W.D. Dorko)

April 5, 1994

Technological Competiveness Symposium: NIST Role, Atlantic City, NJ (W.E. May)

June 14, 1994

NAFTA Environmental QA Planning Meeting, NIST, Gaithersburg, MD (W.E. May)

August 30, 1994

NIST/AIGER Automotive Emissions Research Meeting, NIST, Gaithersburg, MD (W.E. May)

September 15, 1994

Clinical Testing Automation Standards Steering Committee Meeting at AACC, Washington, DC (G. Kramer)

September 23, 1994

Health-Care Technologies for the 21st Century, NIST Strategic Planning Workshop, NIST, Boulder, CO (W.E. May)

V. Process Measurements Division (836)

Gregory J. Rosasco, Chief

A. Division Overview

The Process Measurements Division develops new and improved measurement techniques, sensing devices, instrumentation, standard practices, and mathematical models required for analysis, control, and optimization of industrial processes. Measurements of interest include fluid flowrate (gas, liquid, and cryogenic fluids), liquid density, and volume, humidity, chemical composition, pH, particle properties (size, number density and volume fraction), flow velocity, air speed, temperature, and dynamic pressure, as well as other quantities important in multi-phase reacting and non-reacting process streams. The Division also develops 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, robust computer simulations of processing operations, and requisite chemical, physical, and engineering data.

Accurate measurements for process and quality control require validation of measurement methods and calibration of instruments against, or using techniques traceable to, national standards. Therefore, **calibration services** represent a very important part of our activities, with more than 800 standard tests and calibrations performed this year. These involved air speed, fluid flowrate, humidity, temperature, and liquid density and volume measurements for a wide range of clients across the country.

Maintenance of calibration services at the levels needed by customers is a continuing challenge for the Division. This year, in the **temperature standards** area, we inaugurated cryogenic temperature calibrations utilizing our recently completed low temperature (0.65 to 85 K) calibration facility. This facility now relies on our previously-maintained low-T wire scale and the platinum resistance thermometer calibration facility, but in the future it will be tied to our own realization of the International Temperature Scale of 1990 (ITS-90) in the region below 84 K. We have continued with a multiyear program of modernization and automation of our calibration laboratories. The focus in the temperature area this year was the thermocouple calibration facility. In the case of **humidity standards,** this modernization has the goal of extending the measurement range down to 20 ppb_v (currently we calibrate to 3 ppm_v) in order to enable the semiconductor manufacturing industry to accurately monitor water vapor (considered the most important contaminant) in process gases. This year we constructed a prototype humidity generator which utilizes heat pump and thermoelectric refrigeration, all-metal sealing technology, and eliminates the use of potentially harmful (e.g., CFC) liquid baths. Preliminary testing indicates that this new approach will provide the necessary thermal uniformity and stability to serve as the approach for modernization of all our humidity generation equipment. We have also initiated new approaches to providing standards in the **fluid density and volume** areas this year. In the case of density, we are developing the instrumentation required to measure fluid density via hydrostatic weighing referenced to the accurately known density of single crystal silicon. The goal of this effort is to measure fluid density at or below

30 ppm and to provide high-accuracy (50 ppm) standard reference materials for fluid density. The goal of the fluid volume measurements program is to reduce the uncertainties in our calibrations by a factor of four (to 0.01%) for sizes up to 100 U.S. gallons. This 2-year project is joint with the American Petroleum Institute which has the goal to achieve improved accuracy of fuel transfers in the field.

International intercomparisons and collaborations are an important part of maintaining the U.S. national standards of measurement and this year we had efforts joint with VSL (the Netherlands), IMGC (Italy), CENAM (Mexico), NIM (China), and NRLM (Japan) in the area of temperature. These programs involve comparisons of fixed-point cells, studies of scale non-uniqueness, and comparisons of scale realizations. In another international collaboration, we have worked closely with guest scientists from CENAM with the goal of establishing temperature standards traceable to NIST in this new national metrology laboratory. We are also leading a new effort, with the coordination of the BIPM in Paris, to intercompare humidity standards of the national laboratories of 13 countries.

Our interest in process measurements goes beyond standards to include **sensors and transducers**. Thin film and ultrathin film materials and sensor structures for gases, biological molecules, temperature, and sliding wear are areas of current interest with the Division having disclosed or been awarded seven separate patents in this area in the last year. We have also expanded our effort to develop **micro-sensor arrays** for gas sensing applications. This program is collaborative with the Semiconductor Electronics Division of the Electronics and Electrical Engineering Laboratory. In this effort, SiO_2 bridge structure arrays are made using standard CMOS fabrication technology. Multilayer-film structures containing the necessary electrical connections for signal detection and temperature control are formed on each element of the array. Post processing steps suspend each micro-hotplate element above a pit etched in the silicon chip and add chemical sensing capability with an overlayer of, for example, SnO_2. This approach, combined with the addition of catalytic surface additives, allows control and use of temperature-dependent adsorption/desorption kinetics as a means of tuning the sensitivity and selectivity of individual sensing elements in the arrays. Because of their small size ($\sim 100\ \mu$m), these micro-sensors have very short thermal response times (a few milliseconds) and allow rapid temperature programming with very low electrical power consumption. This year we have demonstrated that temperature programming (for example, application of a regular sequence of short heating pulses with conductivity measurements made at room temperature in the time between pulses) produces high information content responses which allow detection and discrimination among a series of oxygenated species (methanol, ethanol, formaldehyde, and acetone) of interest to the automotive industry. This micro-sensor array technology holds high promise for a wide variety of gas sensing applications with potential for dealing with complex mixtures and hostile environments in a package which is inexpensive, robust, and smart.

Another area of high promise is the use of **self-assembled monolayers (SAMs)** for sensor applications. This year we demonstrated an avidin protein based approach for spatially selective immobilization of proteins on SAMs. This work relied on our previously developed method to photolithographically pattern SAM films with micrometer spatial resolution. Avidin, widely used in bioassays, was shown to bind preferentially to negatively charged monolayers with the added benefit that the avidin on SAM-coated gold substrates showed two to five times greater biological activity than avidin adsorbed on bare gold. This has the potential of enhancing the sensitivity and reducing the costs of biosensors based on the avidin protein.

In addition to the areas of process measurements and control, the Division has a growing effort in **process technology** with a primary focus on the areas of **high technology materials** and **environmental technology**. In the first area, we are principally interested in chemical routes for high volume production of nanoscale materials and the production of semiconductor materials for microelectronic applications. This effort includes thermal chemical vapor deposition (CVD), gas phase etching of surfaces, films, and particles, and plasma processing of semiconductor materials. The research in this area spans a wide range, from computational chemistry to predict thermochemical and chemical kinetic information important to materials formation, through critical measurements of the pathways and rates for selected reaction mechanisms, to the testing of process models on prototypical systems, sufficiently simplified to allow critical tests of the models. In recent years, we have significantly expanded use of computational chemistry. Our work includes ***ab initio* molecular orbital and reaction rate theory** and a very successful project in **molecular dynamics** as a tool for understanding and predicting particle formation and eventually surface chemistry. As a part of this program we develop and/or apply specialized measurement systems, such as our high temperature materials synthesis reactor and the Gaseous Electronic Conference (GEC) reference discharge cell, and state-of-the-art measurement techniques, such as molecular beam mass spectrometry or planar laser induced fluorescence (PLIF). The materials synthesis reactor, utilizing molecular beam mass spectrometry, is being applied to determine mechanisms for the thermal decomposition of a silicon dioxide CVD precursor, tetraethoxysilane (TEOS). The GEC cell is an example of a simplified model system and this year PLIF has been applied to give quantitative, 2-dimensional information about the plasma discharge profile in the cell which will aid in testing chemical models for this system.

Our computational efforts in the process technology area are not limited to molecular level computations. Typically, **computer based process simulations**, including the transport of mass, momentum, and energy, are required to understand, characterize, and control processing systems. The Division has had extensive experience in this area; for example, our work as part of the industry-government Supersonic Inert Gas Metal Atomization (SIGMA) consortium. This multiyear effort was completed this year with the successful demonstration of a control volume model for automated real-time control of this innovative method of forming high technology metal alloys in tailored-size powders. Computer simulations not only translate the predictions of microscopic mechanisms into observable consequences for processing technologies, but often are a vital part of experimental efforts to validate the process models and provide critical chemical and engineering data. For example, we have recently extended computational fluid dynamics (CFD) simulations to improve our ability to accurately meter fluid flows in closed pipes. This work relies on our established data base of velocity profiles (measured by laser Doppler velocimetry) for a wide range of piping geometries and seeks to identify methods for correcting flow meter characteristics to compensate for the flow distortions associated with non-ideal installations. These CFD simulations are also expected to lead to the use of improved technologies for metering. This effort supports our longstanding industry-government consortium on Flow Meter Installation Effects.

In the **environmental technologies** arena, we have a wide spectrum of activities dealing with issues such as halon replacements, emission control strategies, waste destruction, and pollution avoidance. This year we completed development of a new chemical mechanism and associated thermochemical data base for fluorocarbon chemistry, which is important for the rational design and selection of halon alternates for fire suppression and, additionally, is important for modeling the chemistry of plasma etching reactors. The development of this mechanism was a joint activity with the Chemical Kinetics and Thermodynamics Division and relied heavily on computational chemistry. We also continued support of a program in the Building and Fire Research Laboratory in establishing experimental information on extinguishment and dispersion characteristics of potential replacements for halon fire suppressants. The Division's program in reactor engineering in support of waste treatment expanded this year and now includes efforts in the chemistry of supercritical water oxidation (SCWO) studied by *in situ* Raman spectroscopy and measurements of treatment efficiency in a laboratory scale SCWO reactor. This program also involved an assessment of the use of this new technology for treatment of NIST waste streams and continued program support for an Air Force demilitarization program at Tyndall AFB. Our cryogenic engineering expertise was applied in a program to assist the Department of Energy (DoE) in an evaluation of the use of cryogrinding for volume reduction and homogenization of laboratory wastes contained in approximately 200,000 barrels at the DoE Rocky Flats site. This increasing emphasis on the environment is also reflected in the planning for our spray combustion program which in the future will utilize our unique facilities and measurement capabilities to determine the correlation of burner operating conditions, termed "firing practices," to stack emissions. Our experimental program in particle growth, discussed above in the context of production of high technology materials, has also produced a novel approach to the control of unwanted heavy metal emissions in coal combustion. This method enhances the formation of lower volatility products which can form sufficiently large particles to be eliminated by traditional particle control technology. In this work, planar laser induced fluorescence (PLIF) imaging techniques were applied to study the scavenging of volatile PbO by formation of silicates upon injection of gas phase (organo) silicon source. This work is an example of the strong synergy among our various research efforts which integrate chemical knowledge with process models, which include heat and mass transfer, to provide new understanding of and improvements in process and environmental technology.

As part of the expanded responsibilities and revised mission statement of the National Institute of Standards and Technology, the Process Measurements Division continues to expand its interactions with industry. Industrial consortia have been one of the most successful forms of technology transfer, and our "Flowmeter Installation Effects" and "SIGMA" consortia continue to be highly successful. We also have established new Cooperative Research and Development Agreements (CRADAs) in a wide range of technology areas. Our program in **cryocooler technology** has attracted extensive industrial interest with five CRADAs covering areas such as development of compact, no-moving-parts refrigerators for cryoelectronics applications (Tektronix), cryocatheters for surgical applications (Aegis Medical Technologies), and zero-maintenance gas liquefiers for remote well sites (Cyrenco). A CRADA with Morton International/CVD Metalorganics resulted in a successful demonstration of the use of on-line Fourier transform infrared spectroscopy for real-time monitoring of the composition of gas phase metalorganic precursors used in CVD systems. A multiyear CRADA with Babcock and Wilcox has demonstrated the utility of Raman spectroscopic measurements for *in situ* detection of corrosive species in high temperature, high pressure aqueous environments characteristic of boilers and heat exchangers found in electrical power generation systems. Other CRADAs are in place in the areas of nanophase materials processing, accelerated life testing of materials, acoustically driven spray nozzles, and advanced thermally driven waste destruction technology. We have other projects in the Division which are directed at measurements and data important to technologies which have been subjects of ATP awards (these interactions often involve CRADAs). This year we initiated work in support of Microfab, Inc. where our special capabilities in studies of droplet formation, transport, and cooling dynamics could be directed toward problems in solder jet technology. We have initiated a project to utilize our micro-hotplate technology to measure the surface reaction rates for gas phase etching related to an ATP supported effort on dry gas cleaning of semiconductors. Finally, our research on the structure and dynamical ordering of SAMs is being applied to enhance the development of new measurement technology relevant to an ATP project involved with rapid gene classification.

During the past year, the outstanding accomplishments of our technical staff have been recognized with a number of awards. Mr. George Burns, Mrs. Margaret Kaeser, and Mr. Gregory Strouse of our Thermometry Group led a team that received NIST's Allen V. Astin Measurement Science Award for their research and development efforts leading to publication of NIST Monograph 175, "Temperature-Electromotive Force Reference Functions and Tables for the Letter-designated Thermocouple Types Based on the ITS-90," which is the defining document for industrial and calibration laboratory thermocouple thermometry throughout the world. Mr. Strouse also earned a NIST Measurement Services Award for his efforts in producing reference materials for the realization of the ITS-90 in secondary calibration laboratories. A team from our High Temperature Processes Group, Drs. Thomas Avedisian (Guest Scientist from Cornell University), Ashwani Gupta (Faculty Appointee from the University of Maryland), Joseph Hodges, and Cary Presser, received a best paper award from the American Institute of Aeronautics and Astronautics for their paper, entitled "The Role of Combustion on the Transport of Droplets in a Pressure-Atomized Spray Flame," presented at this year's AIAA Aerospace Sciences Conference.

In FY94 the Division was organized into six Groups: Fluid Flow, High Temperature Processes, Reacting Flows, Process Sensing, Thermometry, and Fluid Systems (in Boulder). The following pages describe the activities of these Groups, and their major accomplishments and future plans.

B. Selected Technical Reports (Process Measurements Division)

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

P.J. Giarratano, B.W. Mangum, G.E. Mattingly, and J.R. Whetstone

In the past year, the Division has provided calibration services in response to industry and government requests for assurance of accuracy in fluid flowrate, air speed, liquid density, liquid volume, humidity, and temperature measurements.

Service	Number of items calibrated	
Fluid Flow Meters	28	(24 for industry)
Volumetric Test Measures	58	(54 for industry)
Air speed Instruments	66	(53 for industry)
Reference Standard Hydrometers	40	(20 for industry)
Humidity Sensors	41	(31 for industry)
Standard Resistance Thermometers	64	(53 for industry)
Thermocouples (TCs)	165	(165 for industry)
Laboratory Thermometers	182	(180 for industry)
Potentiometers	2	(2 for industry)
Liquid N_2 Flowmeter Tests	3	(3 for industry)

These calibrations generally establish a traceability link between the national standards maintained at NIST and the standards of the requesting laboratories, thereby providing a basis for accuracy of their measurements. We also establish measurement accuracy via formal Measurement Assurance Programs and round robin tests with individual and multiple laboratories.

Our capabilities, experimental techniques, and facilities are constantly upgraded to meet demands for improvements in measurement services. Activities in the thermometry area include completing the upgrading of the Thermocouple Calibration Laboratory, and commissioning a new low-temperature calibration facility for calibrations of resistance thermometers between 0.65 K and 84 K. Until we have realized the ITS-90 over the entire range from 0.65 K to 84 K (using a new low-temperature facility) and implemented the scale with several capsule-type reference thermometers, the NIST-ITS-90 low-temperature "wire scale" serves as our reference in this region. In the Thermocouple Calibration Laboratory, equipment upgrades and automated control capabilities were introduced which will lead to increased efficiency and accuracy. These include new furnaces, freezing point cells, nanovoltmeters, switch scanners, controllers, and new software. Also, one In, one Sn, two Zn, and two Ag freezing-point cells, each containing 99.9999% pure metal, were constructed and evaluated to increase the accuracy of our Platinum Resistance Thermometer Calibration Laboratory.

We have made efficiency improvements in calibration facilities for the flow of liquid hydrocarbon fluids via upgrades in the software which both controls the calibration conditions and processes the data. These improvements enable automated establishment of the desired test conditions in ways that are significantly better (nominal flowrates are now held to within 1%, a factor of 4-5 improvement) and less (25%) time consuming than previously used techniques. In air flowrate, we continued to improve our pressure, volume, temperature, and time (P, V, T, t) calibration system. New piping systems and diversion valve arrangements have been installed and tested and we have reestablished calibrations for flows up to 15 cubic meters per minute.

2. Liquid Density and Volume Standards

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

We have two new projects to improve liquid density and volume standards. For liquid density measurement, the use of hydrostatic weighing techniques with a silicon crystal as the density standard is a new and viable approach for producing liquid density measurements with improved uncertainties of 30 ppm or better. The equipment for this phase of the program has been procured, and the necessary apparatus has been constructed. This research program also will allow NIST to replace its depleted supply of liquid density Standard Reference Material (SRM) 211C Toluene. Following the determination of the absolute liquid density of a large quantity of ampuled toluene, a density comparator will be used to statistically sample 5 ml ampules of toluene prior to their certification as an SRM with an uncertainty of 50 ppm.

A two-year cost-shared project with the American Petroleum Institute (API) has been initiated to increase the accuracy of the standards used for liquid volume measurement. The objective is to reduce the uncertainty in the calibrated volume of volumetric test measures from the present quoted level of ±0.04% to ±0.01%. The strategy is to use distilled water as a density reference and gravimetric techniques along with more accurate temperature measurements to determine both the contained and delivered volume of test measures. The first phase of the research, which is currently underway, is to determine the feasibility of the method for test measures ranging in size from 1 to 100 U.S. gallons. Preliminary measurements indicate that the accuracy goal is readily attainable for test measures of 5 U.S. gallons and above. The second phase, which will begin in FY95, includes the construction of a new laboratory module with suitable equipment and environmental controls for temperature and humidity. The use of this module will assure calibrations of volumetric test measures at the desired accuracy and will be available to calibration customers thereafter.

3. Flow Measurement and Fluid Systems Research

G.E. Mattingly, J.M. Allingham, P.I. Espina, M.A. Lewis, and J.L. Scott

The Flow Measurement Installation Effects Consortium has the objective of characterizing and improving flow measurement accuracy in "non-ideal" installation conditions for various industrial applications, particularly in the areas of custody transfer of natural gas, oil, and commercial steam. The program uses laser Doppler velocimetry (LDV) in a water flow facility to characterize pipe flows downstream of prevalently used piping configurations; these data are correlated with meter performance at selected locations to allow rational procedures for assuring meter accuracy.

In the past year, the LDV effort has focussed on a generic header configuration. Flow measurement practice in the U.S., especially in the gas and petroleum industries, includes many meter installations downstream of manifolds or headers. The results obtained show that very high levels of pipe flow swirl and severe skewness of the axial velocity profiles can be produced for routine operating conditions. Results also show that these perturbed flows can significantly change the performance characteristics of turbine-type flowmeters (2% changes) and of orifice meters (4% changes). Both of these types of meters are used for custody transfer of oil and natural gas, where tenths of one percent can correspond to significant dollar amounts.

With the goal of developing a predictive basis for improving flowmeter performance, a project to assess the potential of commercially available computational fluid dynamics (CFD) computer codes to model non-ideal turbulent pipe flow has been initiated. We selected the conventional, single elbow and assessed the results using our existing LDV database for the corresponding conditions at a Reynolds number of 10^5. The results were generally quite good. The double eddy swirl pattern and the non-ideal features of the velocity profiles produced by the calculation compare qualitatively very well with those measured experimentally. In terms of the features which are known to correlate with flowmeter performance, the major differences appear in the rate of decay. Quantitative comparisons show differences as large as 12% depending upon the parameter and down stream location. It is believed that this is due to the way the CFD code handles turbulent phenomena. While it is apparent that more effort is needed to improve the quantitative accuracy of this code, CFD does appear to have high promise for modeling 3-D turbulent pipe flows.

This year the final phase of the Gas Research Institute (GRI) sponsored orifice flowmeter research program was conducted at the nitrogen flow facility in Boulder. This multi-year project has focused in recent years on the impact of non-ideal installations on orifice meter performance. All data resulting from these years of research at NIST Boulder and Gaithersburg laboratories, along with data from six other laboratories, were compiled as NIST Database 45, GRI/NIST Orifice Meter Discharge Coefficient Database, which is now available from the Standard Reference Data Program (SRDP). This easy-to-use database provides a convenient, single source of data from the large amount of orifice flowmeter research conducted in recent years around the world.

4. Supersonic Inert-Gas Metal Atomization (SIGMA)

P.I. Espina, G.E. Mattingly, F.S. Biancaniello (MSEL), E. Marx (MEL), S.A. Osella (MEL), and S.D. Ridder (MSEL)

Phase II of the SIGMA project was successfully completed this year. The objective of this project phase was to complete our physical understanding of the dynamics of powder formation in gas-metal atomization and to use this knowledge in the implementation of artificial intelligence techniques for the control and automation of the SIGMA process. The powders produced by this process have unique microstructures with improved strength and corrosion resistance properties which make them prime materials for such demanding applications as turbine blades, power transmission gears, and human prostheses. This industrially attractive project has been partially sponsored by a consortium of American metal powder producing companies for six years because automated production of metal powders has the potential of greatly increasing production yields.

During this last year, an experimental test matrix for the SIGMA process was performed to determine empirical correlations between the various process parameters and the resulting metal powder particle size distribution. These correlations were incorporated into the SIGMA expert control system, and a demonstration of the SIGMA process under fully automated control was performed before an audience of representatives from the consortium member companies. In this demonstration, 23 kg of Inconel 625 superalloy were satisfactorily atomized without operator intervention. The consortium members have requested the initiation of phase III of this highly successful project, which would have as its objective the transfer of the NIST-developed technology to the metal powders industry.

5. Droplet and Spray Diagnostics

J.T. Hodges, C. Presser, and J.D. Allen; A.K. Gupta (Univ. of Maryland); C.T. Avedisian (Cornell Univ.); G. Gréhan and G. Gouesbet (INSA de Rouen)

The dynamics of droplets and particles interacting with gas streams is of particular importance to the efficient operation of industrial combustion systems. To better understand these processes, detailed experimental data are required on properties of droplets and particles dispersed within the gaseous medium, e.g., size, velocity, shape, composition, temperature, and number density, and these must be correlated with desired operating characteristics. This program is moving towards providing these data and correlations while maintaining the requisite level of development of experimental techniques to provide these data, usually via optical methods. The latter effort involves measurements to elucidate physical phenomena and validate computational models for the interaction of light with single droplets, particles, and spray systems.

Fundamental investigations of individual, levitated micron-sized droplets were continued this year. In a study of light scattering from focused laser beams, we have demonstrated significant differences between Gaussian-beam scattering (the most common experimental situation) and plane-wave scattering (the traditional idealization of the scattering) by spherical particles. A first-order correction to the extinction theorem, valid for scattering of a Gaussian beam, was discovered and subsequently validated using a more rigorous and general theoretical approach. These theoretical results led to the demonstration of a new particle size measurement technique based on the forward scattering of a Gaussian laser beam.

In our research on spray combustion, a research swirl burner was used to examine the effect of combustion on the emission of relatively unburnt droplets into the surrounding environment. A two-component phase Doppler system was used to measure the droplet size and velocity distributions at different locations within the spray flame. Time-resolved information was also obtained for the instantaneous values of diameter, and axial and radial velocity components. Combustion was found to reduce droplet number density, droplet deceleration, gas recirculation strength, and droplet entrainment into recirculation regions. As a result, the ability of droplets to penetrate through the flame sheet and into the environment was enhanced despite the presence of combustion air swirl.

The spray combustion program is currently directing its efforts to address issues related to emission of air toxins by industrial combustion facilities. There is a need to correlate the incinerator operating conditions with the spray structure and with the formation of unwanted species. Knowledge of the spray/emission interrelationship will help improve the firing practices of the system, yield financial saving for industry, and reduce regulated emissions.

6. Physical and Chemical Assessment of Halon Alternatives

C. Presser, J.D. Allen, D.R.F. Burgess, Jr., M.R. Zachariah; W. Tsang (833); A. Hamins, D. Baghdadi, P. Borthwick, M.P. Glover, W. Grosshandler, and D. Lowe (BFRL); L. Melton (Univ. of Texas-Dallas), P.R. Westmoreland (Univ. of Massachusetts)

Our support of the Building and Fire Research Laboratory (BFRL) study of potential replacements for the Halon 1301 extinguisher has continued this year. Three gaseous halocarbon agents, identified by the Wright Research and Development Center (WRDC) as the final group of potential extinguishment candidates, were the subject of the study. The agents considered are HFC-125, HFC-227, and CF_3I, along with N_2, which also has excellent suppression characteristics. The results obtained to date are being used to rank these remaining agents as to replacement suitability and, further, are being used by the Air Force for full-scale aircraft fire suppression evaluation.

One experimental study addresses the issues associated with suppression of fires resulting from a broken line in an aircraft-engine nacelle or the splashing of fuel from a ruptured tank in an aircraft dry bay. A turbulent diffusion-flame spray burner facility was assembled and operated to simulate critical aspects of such fires. Experiments were carried out with JP-8 under various operating conditions to determine minimum amounts of agents required to extinguish the spray flame. We determined the agent concentration at extinction for a range of equivalence ratios and elevated incoming air temperatures (up to 350 °C). The most effective agent was found to be CF_3I when considered on a mass basis, except for preheated combustion air (above 65 °F) where performance of all three agents was the same. The performance of HFC-125 and HFC-227 on a mass basis was, in general, the same for the various test conditions.

A confinement chamber was fabricated to study agent suppression capability at elevated pressures (10 to 136 kPa) under confined conditions. Issues of reignition of fuel after flame suppression were also studied. These measurements were made by placing an electrically heated surface 75 mm downstream of the nozzle. Analyses of these studies have not been completed.

During the past two years a major chemical kinetic and fluid dynamics modeling effort was conducted in support of the program to rate potential hydrofluorocarbon, fluorocarbon, and hydrochlorofluorocarbon replacements (HFC's, FC's, HCFC's) for Halon 1301 (CF_3Br), which is the most widely used chemical extinguisher. The modeling program provided a compilation of thermodynamic and chemical kinetic information for a large number of stable and radical halocarbons and oxy-halocarbons; and involved estimation of thermodynamic and chemical kinetic values (when unavailable) using empirical and *ab initio* methods. This has resulted in the formulation of a large comprehensive mechanism for halocarbon pyrolysis and oxidation, modeling of the chemistry under a variety of model combustion conditions, and comparison to experimental results. This work provided significant support to experimental and modeling efforts both at NIST and at other government, university, and industry laboratories.

7. Chemistry of Supercritical Water Oxidation

W.S. Hurst, V.E. Bean, W.J. Bowers, A. Maček, S.R. Charagundla, J.D. Allen, H. Ochel (Humboldt Post Doctoral Fellow), J. Maslar, and A. Lee; J.M.H.L. Sengers (838), and W.E. Allman (Babcock & Wilcox)

This research supports the development of supercritical water oxidation (SCWO), also known as hydrothermal oxidation, as a process for disposal of industrial wastes. Optical techniques have also been developed for *in situ* characterization of chemical species and reactions in high pressure, high temperature water, and the study of corrosion problems in steam boilers.

Two SCWO application projects were initiated this year. The first involves experimental destruction of surrogate shipboard wastes, acetic acid and ammonia, which are known for their resistance to thermal destruction. Thus far, extensive efforts were dedicated to ensuring a highly clean reactor (Hastelloy C276) in order to obtain destruction efficiency data. In the planned series of experiments, test mixtures will be mixed with 100% excess oxidizer (hydrogen peroxide), raised to 25 MPa and subjected to a range of residence times (7-240 s) and temperatures (350-650 °C) in the reactor. The liquid and gaseous effluents will be analyzed by gas chromatography, carbon analysis, and specific ion electrodes. Preliminary data show that all organic carbon in a 900 ppm acetic acid solution can be readily destroyed to better than 99.95%.

In the second project, we have initiated a feasibility investigation of using supercritical water oxidation to destroy NIST-generated wastes. Of the wastes that cannot be re-used or recycled, NIST generates approximately 15,000 liters of hazardous and toxic waste each year which must be incinerated off-site. The composition and quantity of these water-containing wastes has been characterized as being ideally suited for destruction by supercritical water oxidation. Results from this project will not only be used for waste disposal at NIST, but also can serve as a focal point for demonstration of new NIST measurement and monitoring technologies. Further, the practical results generated from these efforts can be transferred to industry where clean-up of dilute waste waters is problematic. Continuing efforts in this area will focus upon using process simulation for design, scale-up and energy budgeting.

Raman spectroscopic measurements of high temperature, high pressure aqueous solutions, which employed the NIST optically accessible flow cell, principally involved two studies. The first study was directed towards elucidation of reaction mechanisms proposed for hydrothermal reactions of low-molecular-weight alcohols. The heterolytic chemistry in the subcritical temperature range generally leads to an improved selectivity over thermochemical reactions which are more likely to occur in a high-temperature, low-density water environment. Hydrothermal reactions of aqueous solutions of ethanol, 2-propanol, and *tert*-butanol, in water at temperatures from 150-500 °C and a constant pressure of 34.5 MPa, were observed with spontaneous Raman spectroscopy. At temperatures up to 450 °C, only dehydration products could be detected, whereas at 500 °C, cleavage was observed. These studies demonstrate for the first time that conversion of low-molecular-mass alcohols to alkenes occurs not only up to quite high temperatures but also with high conversion rates. The second study investigated the utility of Raman spectroscopy for *in situ* identification and quantification of contaminants and chemical additives of interest to the steam and power generation industry. This work has developed into a collaborative research effort with Babcock & Wilcox and Electric Power Research Institute (EPRI). Currently underway are studies of the effectiveness of diamond-like coatings on sapphire to provide robust windows for corrosive aqueous environments.

Control and knowledge of the corrosion of reactor surfaces is one of the key elements for the successful application of SCWO technology. The feasibility of using Raman techniques for the study of corrosion mechanisms on metal surfaces has been demonstrated, with the detection *in situ* at high temperature and pressure of the growth of various mixed oxides and spinels on stainless steel surfaces. Further work will focus on the behavior of selected metal alloys in various corrosive high temperature and pressure environments.

8. Measurements Support for Semiconductor Technology

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Support for semiconductor technology addresses several manufacturing process areas: plasma processing (primarily etching), chemical vapor deposition (CVD) of thin films, and measurements for process-gas purity. Accurate measurements and data are required to support and validate predictive models used in the development and operation of plasma and thermal reactors in semiconductor manufacturing. Our efforts in these areas have included the development of accurate techniques for the measurement of RF voltage and current and the correlation of kinetic-energy distributions of mass identified ions with optical characteristics of the plasma. These measurements rely on the Gaseous Electronics Conference (GEC) RF reference cell as a test bed for calibration/development of diagnostic measurements and data. This year we have applied planar laser-induced fluorescence (PLIF) imaging to provide quantitative (relative) two-dimensional information on the argon $1s_5$ (a metastable state) density distribution in the GEC cell. Comparison of centerline metastable argon and optical emission profiles indicate that metastable state distribution is largely determined by spatially dependent electron-impact excitation. While these measurements provide information on plasma interactions, they principally demonstrate the feasibility of the PLIF technique, and our real interests are in measurements on reactive gases. Data from this technique also will be combined with our accurate RF measurements as a means to investigate ion dynamics, particularly ion energies, resulting from acceleration across the plasma sheath toward the wafer surface. This information is important to determining mechanisms of surface damage, an increasingly important processing issue.

Activities in the thermal CVD area involve both critical data for processing and measurement techniques for process control. The former involves a recently established collaborative effort with SEMATECH and the Chemical Kinetics and Thermodynamics Division to determine decomposition mechanisms and rates for two critical reactants used in CVD systems, tetraethyoxysilane (TEOS) and phosphine, in the presence of silane. This is a combined experimental and computational chemistry effort to determine initial decomposition mechanisms and their associated rate data. In the area of process control, we have worked on control of the reactants in metalorganic chemical vapor deposition (MOCVD) systems. To consistently fabricate high quality CVD components, feed stream composition must be accurately controlled; however, there are no commercially available, on-line technologies which can quantify these mixtures satisfactorily. As part of a CRADA with Morton International, we have established the feasibility of relating the measured infrared (IR) absorbances to actual mixture concentrations within 1% and in real-time (1 Hz). In this work, we assembled an optically-accessible MO flow system (similar to that used by the semiconductor industry) and conducted on-line Fourier transform infrared (FTIR) absorption measurements of various single and binary MO/inert-carrier gas flows. Binary mixtures of trimethylaluminum (TMA) and triethylgallium (TEG) were examined over the industrially relevant 200-14,000 ppm (by mass) concentration range. Compositional information was acquired in two sequential steps: data acquisition and data processing. The 1% quantitation level was achieved in nearly real-time by using a coarse resolution, 16 cm^{-1}, with scan times of only 0.25 s (4 Hz). In the second step, the spectra were retrieved from the data system and analyzed via user-defined macros to determine concentrations. On our system, this step took about 30 s; however, efforts were not made to automate or optimize the cumbersome PC-based data processing procedure and it is felt that processing times can be reduced to a few seconds. Based on the results of this feasibility study, there are immediate opportunities to incorporate this FTIR technique for CVD process measurement and control. As a possible alternative, based on the coarse resolution requirements, a simple photometer or filtering arrangement could replace the need for acquiring an entire spectrum of information. This would have obvious data processing speed and storage benefits and would reduce the cost and complexity of the system.

Moisture, one of the most prevalent contaminants in process gases, contributes more significantly than any other contaminant to device rejection and reduced productivity. New processes used for fabrication of sub-micrometer scale devices require humidity levels at the 15 ppb_v level; however, current water vapor concentration measurement standards are limited to concentrations above 2 ppm_v. Improved standards are needed to provide a sound basis for evaluation of existing measurement technology and development of improved measurement methods. As part of this effort, we are investigating the use of near-infrared (laser) absorption which utilizes an optical "ring down" method adapted from optical component characterization techniques. Effective absorption path lengths of several kilometers are obtained, thereby providing high sensitivity at low concentrations. This system will be coupled to our low frost point humidity generator (providing moisture concentration levels down to 15 ppb_v), which is nearing completion. This generator will be used to determine the value of fundamental optical constants that may serve as the operational basis for low moisture concentration measurements extending to the ppb range and perhaps below.

9. Special Topics in Waste Treatment

S.R. Charagundla, A. Maček, and N.R. Quick (EG&G-Rocky Flats);
J.D. Siegwarth, J.L. Scott, M.A. Lewis and P.J. Giarratano

Structural materials used in hazardous waste incinerators have been known to fail prematurely because of the severity of the environment. To address this problem, EG&G-Rocky Flats has joined us in a collaborative effort to develop a fluidized bed unit for use as a materials accelerated life tester for screening candidate structural materials. A series of tests to screen candidate alloy coupons was completed during this past year. Currently, work is in progress to test and evaluate industrial filter elements exposed to high-temperature Cl-containing hazardous environments. In addition, EG&G is interested in developing and implementing an *in situ* corrosion monitoring technique. In response to this requirement, a bench-scale materials accelerated life tester was designed to investigate the *in situ* application of Fourier transform infrared (FTIR) spectroscopy. This technique will be used to provide absorption spectra at different stages of the corrosion process. Changes in the spectral profiles with time will be used to characterize the formation of material corrosion. Work is currently in progress to assemble the apparatus, and a test of the feasibility of the *in situ* corrosion monitoring concept will be completed in FY95.

The disposal of a barrel of DOE-Rocky Flats soft waste requires that the kind and amount of contained hazardous metals and solvents be known, at a single sample analysis cost of $10,000. Since the waste is in separate bags of varying composition it is anticipated that four samples will be needed for one barrel. There are presently 200,000 barrels, with many more expected from site cleanup. An alternative approach, proposed by DOE-Rocky Flats, to the current sampling method is to first grind and homogenize the barrel contents so that one sample per barrel would be sufficient. This leads to reduced cost as well as significant reduction of waste volume. To insure that solvents in the waste are retained for analysis and to enhance friability of the materials, it was suggested that the contents be cryogenically cooled during the handling and reduction processes. As a result of our expertise in cryogenic engineering, we were contracted to explore the feasibility of cryogrinding the waste. We have investigated numerous commercially available methods and equipment for grinding materials with the intention of identifying suitable equipment that could be modified for cryogenic service. Tests using a screened shredder confirmed that a shredder serving as a preprocessor and a feeder followed by a granulator offers a viable means of reducing soft waste. Cryopumping to remove solvents from the waste prior to grinding has been found to be impractical. An approach based on retaining the solvents in the waste during grinding with homogenization, sampling, and subsequent analysis has been suggested. Based on these findings, we completed some preliminary handling and processing system designs utilizing a shredder and granulator in series. Operating the reduction and handling facility in a cryogenic environment that will be integrated into a prescribed Rocky Flats glove-box placed stringent requirements on the design. A very reliable system is desired to minimize the need for intervention from outside the glove-box. While the NIST effort will continue in FY95, the level and detailed work plan are being revised based on current results.

10. ATP Intramural Research Support

I - C. Presser, A. Maček, J.T. Hodges, and K. Kreider; M. Moldover (838); C. Handwerker and F. Gayle (MSEL); B. Murray (CAML); D.B. Wallace (MicroFab); C.T. Avedisian (Cornell Univ.);
II - M.J. Tarlov, G.E. Poirier, and G. Gillen (837);
III - D.R.F. Burgess, Jr., R.E. Cavicchi , G.E. Poirier, M.R. Zachariah, J.R. Whetstone; J.S. Suehle and M. Gaitan (EEEL);
IV - G.E. Mattingly, G.P. Baumgarten, and P.I. Espina; A. Kornhauser (Virginia Polytechnic Institute and State University); R. Hrbek (Calmac Mfg. Corp.)

Four separate projects were conducted this year in support of ATP awardees; these are discussed in the following:

I. MicroFab Technologies is developing a new solder application technology for the electronics industry. This method is based on ink-jet printing technology to produce and accurately place molten solder droplets of 25-100 μm diameter. A CRADA was established this year in conjunction with MSEL and CAML to provide measurement technology, data, and models in support of ink-jet based solder dispensing systems. During the past year, meetings with MicroFab resulted in identifying two areas of collaboration, 1) visualization of solder droplet in-flight dynamics and impact, and 2) measurement of droplet cooling and spreading over a surface following impact using thin-film thermocouples. The significance of these two topics is to better understand and control the droplet impaction process and improve solder/surface adhesion. Research in the latter area is expected to begin in the coming year.

II. The ATP-sponsored Genosensor Consortium is attempting to develop a microelectronic chip containing large arrays of DNA probes for the rapid sequencing of DNA. In support of this effort, we are examining the structure of covalently bound DNA probes on self-assembled monolayer (SAM) surfaces on gold. We employ the surface sensitive techniques of x-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), and secondary ion mass spectrometry (SIMS) to examine the SAM-bound probes which consist of short, single-stranded DNA segments having nine nucleotides (9-mer). Two different covalent immobilization chemistries were examined, carbodiimide and a proprietary surface modification procedure. In both cases, it was found by monitoring the XPS N 1s core level that the coverage of bound DNA increased with increasing concentration of the DNA probe reaction solution. SIMS also proved to be a very sensitive technique for relative quantitation of a surface confined probe where parent ion signals for the four different nucleotides (T, C, A, and G) were detected. These experiments show that SIMS may be a promising technique for assessing the quality of large DNA probe arrays. STM results indicate that the probes bind preferentially to step-edge regions of the gold substrate indicating that coupling reactions may proceed with greater facility in defective regions of the surface.

III. In the last two years, we initiated a research project involving a new technique specifically designed to measure rapidly the products and the rates of surface etching processes. This work was in response to an ATP grant to FSI International to develop a dry (gas phase), reactive etching process for use as a chemical cleaning step in silicon wafer fabrication. With the push for smaller and higher quality devices, it will be necessary to replace some wet chemical and plasma etching processing steps (which have a number of limitations) with purely gas phase processes. Our novel measurement scheme employs phase-sensitive mass spectrometer detection of desorbed etched products from substrates which have been temperature modulated by means of micro-hotplate arrays. In a preliminary experiment, we have demonstrated the utility of this approach by measuring the desorption kinetics of a simple system (CO/Pt). An experimental system has been designed to develop this new approach systematically. Construction and testing will proceed in the coming year and, if successful, we believe that this technique should be very useful for rapidly obtaining surface reaction rate data for a wide variety of surface chemical processes.

IV. Calmac, Inc., and its academic affiliate, the Virginia Polytechnic Institute and State University (VPI & SU), have the goal to optimize a multiphase ejector expansion refrigeration cycle (EERC) through the design of special ejector nozzles and the selection of refrigerants. Our efforts in support of this program have included the design and construction of transparent nozzles to enable flow visualization studies of the critical two-phase flow fields in the new ejector geometries. We have also worked extensively to resolve unforeseen flow measurement problems in both the gas and liquid flow portions of the EERC test facility. These included conducting several special liquid and gaseous flow metering tests to clarify problem sources. The results have shown the need for new types of flow meters; these changes are being made and NIST calibrations of the new meters in the special pipework are planned for FY95. The visualization studies currently await scheduling at the VPI & SU test site but are expected in FY95.

11. Application of Computational Chemistry

M.R. Zachariah, D.R.F. Burgess, Jr., M.J. Carrier, W. Tsang (833), E. Blaisten-Barojas (George Mason Univ.), V. Bedanov (Institute of Theoretical and Applied Mechanics, Novosibirsk), P.R. Westmoreland (Univ. of Massachusetts), and C. Melius (Sandia National Laboratories)

The application of computational methods (that span the range of atomistic to detailed chemical kinetic modeling) for data generation and process simulation has become a very important component in the effort to characterize reacting flows. Work has continued this year on the generation and evaluation of a self-consistent data base for fluorocarbon thermochemistry based on *ab initio* molecular orbital theory. Thus far, over 90 species have been calculated and compared with 44 literature-cited species heats-of-formation leading to an average deviation of 6.7 kJ/mol, which is very nearly equivalent to the uncertainty in typical measurements of rates of reaction. Work is currently underway to evaluate rate constants for reactions calculated from a combination of *ab initio* methods and reaction rate computational methods. These data are important in understanding the combustion of fluorocarbons, both for environmental consequences and for replacement of halon fire suppressants, as well as for developing mechanistic models for plasma etching reactions.

We have also begun the development of a computer based solution to the problem of isomerization, with multiple exit channels. This computer code, which involves solution of the time dependent master equation, will lead to a powerful new tool for self consistent evaluation of rate constants directly from *ab initio* methods for a reaction manifold.

We also are continuing our work applying molecular dynamics methods to the problem of cluster-cluster and cluster-surface processes. The goals are to understand particle formation and deposition in CVD reactors, from a microcontamination perspective, and particle formation for synthesis of nanostructured materials. In these calculations, realistic atomic-level interaction potentials are used to calculate the classical reaction trajectories and equilibrium properties of spatially confined systems. This year these calculations have been used to obtain surface and bulk contributions to the energy for silicon clusters as well as to extract fundamental parameters, such as surface tension, binding energy, and internal diffusivity, all of which are critical to developing and specifying process models for particle and surface growth. Work is ongoing to develop a parallel dynamics code that can be used to compute problems with a larger number of atoms.

12. Synthesis and Characterization of Nanostructured Materials

M.R. Zachariah, M. Aquino-Class, C. Amato-Wierda, B. Shull (MSEL), J. Maslar, B. McMillin, E. Steel (837), and P. Biswas (Univ. of Cincinnati)

This area focuses on the development of bulk methods for the vapor phase growth of nanostructured materials as well as the fundamentals of the chemistry and physics of nanoparticle formation. After a long development, a high temperature, low pressure materials synthesis flow reactor, coupled to a molecular-beam mass-spectrometric sampling system, has been brought on line. The first study has been the pyrolysis of tetraethoxysilane, a precursor used in the growth of SiO_2 films. Current measurements suggest that the primary mechanism for decomposition involves concerted elimination of ethane. Our interest is in both quantitative kinetics for pyrolysis and oxidation and a mechanistic understanding of the particle formation process from a chemical perspective.

This year, in a joint project with the Materials Science and Engineering Laboratory, we have demonstrated a flame processing method for the bulk production of a unique nanoscale microstructure with superparamagnetic properties. The objective of the work is to synthesize materials that would have the potential to extend the efficiency of current magnetic refrigeration systems. The material consists of discrete ferromagnetic clusters (5-10 nm) of γ-Fe_2O_3/Fe_3O_4 encapsulated within a nonmagnetic (SiO_2) host particle of 30-80 nm in diameter. The nonmagnetic host serves to separate the magnetic clusters sufficiently such that no long-range magnetic ordering occurs until an external magnetic field is applied; then all the magnetic spins align, resulting in a lower system entropy and rejection of heat. The optimum material we have developed to date is superparamagnetic from 155 K to room temperature, a good level of performance. Future work will explore bulk synthesis of complex ferrites and new techniques for particle coating.

To develop and test models for the production of these nanocomposites, we have begun an effort on *in situ* characterization during particle formation. This year we applied the 2-dimensional techniques, planar Mie scattering for particles and planar laser-induced fluorescence (PLIF) for chemical species. PLIF measurements on vapor phase FeO in the system for growth of superparamagnetic nanocomposites showed that the chemistry of precursor decomposition occurs at the flame front, as seen by a rapid rise in the FeO concentration, followed by a slow decay as FeO nucleates. Interestingly, co-injection of the silicon precursor does not alter the FeO concentration, indicating that the gas phase nucleation of the SiO_x and FeO_y are independent of each other. These observations will guide the modeling of this multiphase combustion synthesis system.

Work in a similar vein had been directed toward the development of approaches to the control of heavy metal (Cd, Hg, Pb) emissions during coal combustion. The approach used has been co-injection of a scavenging agent which forms a lower vapor pressure metal containing species, thereby enhancing the nucleation rate and producing a larger particle that can more easily be removed. By controlling temperature and co-injecting a silicon precursor, the formation of Pb-silicates has been promoted which, we have shown, leads to an 80 % decrease in the PbO emissions. Again in this case, *in situ* optical measurements confirmed the proposed mechanism.

13. Thin Film Sensor Development

K.G. Kreider and A.W. Ruff (MSEL)

Efforts in this program have been primarily in two areas, (1) development of thin film thermocouples for use at high temperatures and (2) initiation of a project to develop thin film wear sensors for application to rotating shaft bearings. The stability of silicides in high-temperature oxidizing environments and their excellent electrical conductivity make them attractive candidates as thin film thermocouple materials. Characterization of the performance of sputter-deposited thin films of $MoSi_2$, $ReSi_2$, $TiSi_2$, $TaSi_2$, and WSi_2 as thermoelements were obtained at temperatures to a maximum of 1200 °C. A multilayer technique was developed to ensure constant silicon stoichiometry during oxidation to maintain a constant Seebeck coefficient. $MoSi_2$ and $TiSi_2$ on Al_2O_3 substrates demonstrated feasibility for high temperature applications where corrosion resistance is desired and where traditional metal thermocouples are vulnerable to deterioration.

Under the sponsorship of the Office of Naval Research, a collaborative effort with MSEL began this year to investigate thin film wear sensors. Structures have been fabricated of alternating conductive and insulating layers. Materials selection and sensor fabrication studies have included SiO_2, TiO_2, and Al_2O_3 as insulators with various metals and $TiSi_2$ as conductors. Although an optimal materials combination has not been found, good results have been obtained with $TiSi_2$ on Al_2O_3 in ring and block wear tests. A linear change in DC resistance as a function of wear depth is observed. Future efforts will focus on improved thin film materials selection.

14. Gas Sensing with Micro-Hotplate Sensor Arrays

S. Semancik, R.E. Cavicchi, G.E. Poirier; M. Gaitan and J. Suehle (EEEL); T. McAvoy (Univ. of Maryland)

A primary goal of our expanding program on sensing of gaseous species is to develop the science and technology for producing a new generation of faster, more versatile and reliable gas sensors. Although many different solid state sensing principles may be pursued, this effort focuses on adsorbate-induced conductance changes in semiconducting oxide-based materials, e.g., tin oxide (SnO_2). In this approach, the advantages of conceptual simplicity are combined with use of robust, high quality materials to achieve a conductometric device amenable to incorporation into sensing arrays. The objective is to develop a commercializable, generic technology to impact a number of large market areas, e.g., industrial process control, pollution prevention, and environmental monitoring. To achieve this goal, our film growth and gas sensing technological capabilities are combined with silicon micromachining and integrated circuit fabrication expertise in EEEL.

CMOS (complementary metal oxide semiconductor) fabrication provides the means to develop multi-layer pixel structures capable of achieving controlled temperatures to ~800 °C, with 1 ms response time. These pixels are easily incorporated into gas sensing arrays. Arrays are critical for determining individual component concentrations in multi-component gas mixtures because individual sensing elements are not perfectly selective. An array of sensing elements having varying sensitivity and selectivity to each component of the gas mixture of interest provides the means to measure concentration of individual components. Selectivities and sensitivities must be known and well differentiated for gases of interest and for interferants, both singly and in combination. This is accomplished by constructing pixels having significantly different response to each component of the mixture. Temperature programming of individual pixels provides a powerful tool to achieve response differentiation. Single pixels with a SnO_2 sensing film having a surface-dispersed (approximately 2 equivalent monolayers) palladium (Pd) catalytic additive provided well-differentiated response characteristics. Temperature programming consists of heating the sensing film to temperatures ranging from near ambient to approximately 500 °C for 100-500 ms at various duty cycles. The electrical conductance of the sensing film is then measured shortly after the heating pulse when the pixel temperature has returned to ambient temperature. A typical thermal program increases maximum pulsed pixel temperature in several steps from ambient to 500 °C. Using this method conductometric response to ethanol, methanol, acetone, and formaldehyde have significantly different response patterns. These patterns have high information content that presents a challenge to new signal processing algorithm development. Advantage can be taken of recent developments in neural networks to address this issue. A collaboration has been developed with the University of Maryland for algorithm development with initial results demonstrating quantitative response to CO in air for concentrations between 3 and 100 ppm.

These results have been obtained in the face of considerable difficulty in achieving low noise electrical contacts to the sensing film. The electrical contact material, aluminum, is severely damaged during the final micro-machining step. A multiple step procedure has been used to correct this damage. It is time-consuming and not compatible with IC production methods. Investigation of alternatives have included the use of tungsten for metallization. Discussions of collaborative efforts with the Microelectronics Research Laboratory (MRL) of the National Security Agency have begun. MRL is a fully capable IC manufacturing laboratory able to make sensing arrays using tungsten as the metallization material. Initial tests of tungsten films on silicon show that the film is not attacked by the micromachining etchant.

In the coming year an investigation of the sensing response of films other than SnO_2, e.g., WO_3 and ZnO, as well as mixed metal oxide films, e.g., TiO_2/MoO_3, TiO_2/WO_3, and TiO_2/Nb_2O_5, over a mixing ratio range, will be pursued. Optimization of surface-dispersed catalytic additives to enhance sensing response will be examined, and sensing response pattern recognition algorithms for both species detection and concentration measurement (collaborative with the University of Maryland) will be developed. The response of single pixels and arrays to multi-species mixtures will be characterized, and a broader range of thermal programming methods to enhance response differentiation will be studied. On-chip/in-package circuitry to support array operations and a robust tungsten metallization process will be developed.

15. Self-Assembled Monolayers for Biosensing

M.J. Tarlov, M.E. Collison, G.E. Poirier, G. Gillen (837), M. Lewis (831), W. Knoll (Max-Planck-Institute for Polymer Science, Mainz, Germany)

This project is focussed on chemical and biological sensing applications of alkanethiol self-assembled monolayers (SAMs) of the general formula $X(CH_2)_nSH$. The thiol headgroup attaches strongly to gold surfaces to form densely packed assemblies yielding a surface comprised of the terminal functional group X. By varying the identity of X, surface chemical and physical characteristics can be customized to control adsorption processes and impart chemical recognition properties to SAMs. We have shown that UV photolithography is useful for patterning SAMs with micrometer resolution; however, relatively little is known about the photochemical mechanism. To better understand this process, we have used surface enhanced Raman spectroscopy to monitor the C-S, C-C, and S-O stretching regions as a function of UV exposure time. It was determined that the major steps in the photolysis reaction are scission of the C-S bond, followed by desorption of alkyl chain fragments, and then oxidation of the remaining adsorbed sulfur. The desorption step appears necessary to allow close approach of O_2 to sulfur so that oxidation to a sulfonate may occur. Future efforts will determine the optimum (in terms of photospeed) wavelength for the patterning process.

We are interested in exploiting avidin-biotin as a means of attaching biological material to SAMs. This year we investigated the adsorption of avidin on SAMs and focussed on negatively-charged and hydrophobic monolayer surfaces because many bio-sensors and bio-assays use avidin adsorbed on such layers. Photopatterning was used to prepare the surfaces which were then exposed to avidin solutions having salt concentrations that promoted avidin adsorption on negatively-charged regions while simultaneously retarding adsorption on hydrophobic regions. Secondary ion mass spectroscopy images confirmed the preferential adsorption, thereby demonstrating that SAM technology will be useful in creating patterned biomolecular arrays. In a related effort, a collaboration with the MPI-Germany, streptavidin binding to photopatterned biotinylated alkanethiol SAMs was imaged *in situ* using surface plasmon microscopy (SPM). Micrometer-scale patterns of a mixed biotin- and hydroxy-terminated monolayer were formed in an inert, hydroxy-terminated alkanethiol monolayer using a UV-photopatterning procedure. Using SPM, contrast is readily observed where streptavidin specifically binds to the mixed termination regions. This approach may prove useful for the parallel interrogation of surface bioarrays.

The molecular structure and ordering of SAMs is of great interest and this year we have used scanning tunneling microscopy (STM) to focus on the dynamics of the ordering of alkanethiol molecules on Au(111) single crystals. It was found that long-chain octanethiol and decanethiol SAMs form a densely-packed c(4x2) overlayer, while short-chain thiols exhibit both a liquid-like and a lower coverage $p \times \sqrt{3}$ "pinstripe" phase. A characteristic common to all SAMs examined is the presence of single-Au-atom-deep pits, formed during the self-assembly process, whose concentration largely determines the size of ordered alkanethiol domains. The STM was used to observe the ordering of butanethiol monolayers in real time. The monolayer spontaneously crystallizes via homogeneous nucleation from a liquid-like phase and grows into a complex domain network. In the presence of the liquid phase, facile diffusion of gold is observed, whereby the pit number density and size distribution changes in a manner consistent with an Ostwald ripening process in which large pits grow at the expense of small pits. When the monolayer completely crystallizes to the lower coverage, pinstripe phase redistribution of gold atoms ceases. This understanding is vital for assembling more stable and defect-free monolayers.

16. Advanced Refrigeration for Cryogenic Systems

R. Radebaugh, P. Bradley, E. Marquardt, and M. Lewis; G. Swift (Los Alamos National Laboratory); J. Gary and A. O'Gallagher (CAML); K. Kapkin (Univ. of Colorado); F. Kuriyama (Ebara Corp., Japan); D. Friend and M. Huber (838)

This program has a number of projects focused on technology-enablers for cryocoolers: cryogenic refrigerators, their associated regenerators, and compressors. A major part of the program this last year was a continuation of a CRADA with Tektronix with the goal of developing a refrigerator with no moving parts to cool superconducting electronics. This unit is based on a thermoacoustically driven (TAD) orifice pulse tube refrigerator (OPTR). During FY94, a 100 Hz TAD (designed and built by Los Alamos National Laboratories) was assembled and shown to produce the desired pressure ratio of 1.20 with no load. We worked closely with Tektronix on testing and improving the 100 Hz OPTR system. At the conclusion of these tests, their one-stage system reached a minimum temperature of 100 K and produced 10 W of refrigeration power at 109 K. These results are close to the design values, indicating a good understanding of the design issues for the higher frequency systems and setting the stage for the realization of the planned 400 Hz refrigerators. This year the program emphasis was shifted to the development of a two-stage (400 Hz) system for a temperature of 50 K, rather than the previous four-stage, 10 K system. The higher temperature is adequate for high temperature superconductors, the new focus for the Tektronix effort. We have designed an improved regenerator for the second stage of this 400 Hz OPTR using glass microchannel plates with 25 μm diameter holes. We have assisted Tektronix in the design of the 400 Hz OPTR and have helped analyze the data from a one-stage 400 Hz TADOPTR that reached a low temperature of 147 K. Plans for FY95 include constructing and testing the microchannel plate regenerator for the second stage and helping Tektronix analyze the data on a two-stage 400 Hz TADOPTR.

We also continued work on a project to test the feasibility of producing refrigeration at 4 K with an orifice pulse tube refrigerator. The work is funded in part by the Naval Surface Warfare Center for the purpose of cooling a superconducting magnet to use in their mine sweeping program. During FY94, the complete three-stage pulse tube refrigerator was designed and all parts were fabricated. The third stage uses Nd spheres in the regenerator to provide the necessary high heat capacity. The system will be completed and tested early in FY95.

A small program (with NASA funding) to develop design methodology for highly efficient linear resonant compressors or pressure oscillators to be used to drive pulse tube or Stirling cryocoolers continued this year. We have finalized the design procedure for the flexure bearings, constructed a flexure bearing assembly, and tested it for 2×10^6 cycles with no sign of fatigue. Plans for FY95 are to finish construction of the compressor and test it, if funding becomes available.

We have begun a project, funded by Lockheed, to design both an 80 K and a 60 K pulse tube refrigerator using a coaxial configuration. The coaxial configuration has the advantage of a compact package. There are uncertainties regarding the effect of radial heat transfer between different components in the system that are to be investigated in this work. We have completed the design of the 80 K coaxial pulse tube refrigerator including the machine drawings for all parts. Plans for FY95 include construction, testing, and validating the design concepts for this new type of pulse tube refrigerator (for 80 K) and the completion of the design of the 60 K refrigerator.

A CRADA has been established with Cryenco Sciences, Inc. to develop pulse tube technology for application to liquefying natural gas at unattended sites. A 2000 liter/day liquefier is being designed that uses some of the natural gas (about 30%) to fire a burner to power a thermoacoustic driver (TAD), which in turn drives an orifice pulse tube refrigerator (OPTR) that liquefies the rest of the gas. Our collaborators from Los Alamos National Laboratory are providing the expertise on the TAD. To date we have optimized the operating conditions of the two pulse tube and regenerator stages for this system and have provided Cryenco with an approximate layout drawing of the OPTR part of this system. There are new challenges that must be overcome in designing a system of this large size that we have not experienced previously in small systems, such as minimizing pressure drops due to radial gas flow in reducers with large diameter changes. Plans for FY95 include completing the design of the OPTR for the 2000 liter/day liquefier.

A CRADA has been established with Aegis Medical Technologies to help them develop a 3-mm diameter catheter in which the tip can be cooled to about 120 K for freezing damaged heart tissue that causes heart arrhythmias (irregular heart beats). We have optimized the working fluid to be used in a Joule-Thomson expansion at the tip. It is a mixed fluid with five components. We also have designed a miniature heat exchanger to fit in the tip of the catheter and are currently discussing the construction with various photofabrication companies. Plans for FY95 include constructing and testing of a 3-mm diameter catheter.

17. Implementation and Dissemination of the International Temperature Scale of 1990

C.W. Meyer, W.L. Tew, O. Tamura (NRLM), D.C. Ripple, G.W. Burns, G.A. Evans, Jr., M.F.G. Kaeser, G.T. Furukawa (Guest Researcher), G.F. Strouse, E. Martines-Lopez (CENAM), Y. Liu (NIM) and B.W. Mangum

A major focus for this project is completion of an accurate realization of the ITS-90 as it is defined below 83.8 K. Currently, the NIST-ITS-90 low-temperature "wire scale" serves as the NIST reference for calibrations in the region 0.65 K to 83.8 K. This year some ranges of the ITS-90 and some of the seven fixed points used in defining the scale between 0.65 K and 83.8058 K were realized in our new scale-realization facility. Preliminary results from realizations at the e-H_2 vapor-pressure fixed points at 17.035 K and 20.27 K by H_2 vapor pressure thermometry differed from the wire scale by as much as 0.3 mK. These discrepancies are outside expectations and will be subject to further investigation. We have also conducted a preliminary comparison of our realization with that of NRLM in the range from 1.25 K to 4.5 K. Differences as large as 7.5 mK were observed; these have been attributed to lack of a sufficiently accurate calibration of NRLM's pressure transducer.

Construction of a high-purity gas-handling system for preparing sealed, transportable cells to be used for realizing the triple points of the ITS-90 at temperatures between 13.8 K and 84 K (and some secondary points at intermediate and higher temperatures) neared completion. 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.

To ascertain how closely our realization of the triple point of water (**the reference point of the ITS-90 and** the temperature of which **determines the size of the unit of temperature**) agrees with those of other nations, we have intercompared our cells with two cells constructed at CENAM, and currently we are intercomparing our cells with two cells constructed at NIM. In all cases, the NIST reference cells, to within our reproducibility of 0.02 mK, are of equal or superior quality. Next year, we will participate in a round robin, organized by the BIPM under the aegis of the CCT, involving triple point of water cells of various constructions from several other countries.

Efforts to determine the non-uniqueness of the ITS-90 in the ranges 631 °C to 962 °C and 20 °C to 630 °C were continued this year. These data are required in order to establish realistic uncertainty statements for calibrations. Since a large sample of high temperature standard platinum resistance thermometers (HTSPRTs) is required for this study and since our supply of HTSPRTs is inadequate for the range 631 °C to 962 °C, we organized a collaborative effort with the national laboratories of Italy (IMGC) and the Netherlands (VSL). HTSPRTs for this investigation were selected, based on their stability upon high-temperature exposure, and all 10 NIST HTSPRTs to be used in this collaboration have been calibrated from 0 °C to 962 °C. The comparator for the experiments is undergoing final evaluation and adjustments prior to beginning the comparison measurements.

In recent years, we have had a significant effort in developing Standard Reference Materials (SRMs) for fixed-point cells, with the goal of disseminating the ITS-90 to secondary calibration laboratories. In this effort, the melting/freezing behavior of three Al freezing-point cells, containing 99.9999+% pure Al, was evaluated as part of the certification process of the Al for use as SRM 1744, the Aluminum Freezing-Point Standard. The freezing-point temperatures of the three Al cells (660.323 °C) were highly reproducible and agreed to within 0.1 mK. Other features of the melting/freezing curves also indicated the Al to be of extremely high purity. SRM 1744 is now available for purchase. We have also produced metrological quality fixed-point cells for CENAM. In this collaboration, two cells each of Ag, Sn, In, and Ga were constructed and evaluated for their Thermometry Group.

18. High Temperature Thermometry Research

G.W. Burns, D.C. Ripple, V. Martinez-Fuentes (CENAM) and B.W. Mangum

Research in this area is concentrated on thermocouples (TCs). Continuing the investigation of Au/Pt TCs, 12 new TCs were constructed from five lots of Pt and Au of 99.999% purity. Six TCs were tested and found to have emf's at the Ag freezing point (962 °C) that were within a band of + 25 mK to - 80 mK relative to the NIST-determined Au/Pt reference function value. This is exceptional for TCs and means that **without calibration**, Au/Pt TCs constructed of high-purity materials could be used for temperature measurements up to 1000 °C with inaccuracies no greater than about ± 0.1 °C. This is at least a factor of two better than can be achieved with **calibrated** type S TCs, which currently serve as the standard for industry.

As part of our effort to develop new TCs as reference thermometers and as fairly-inexpensive, high-stability, high-temperature thermometers for industrial use, studies of the emf stability and repeatability of Pt/Pd TCs for different methods of annealing wire of different purity continued this year. Fourteen Pt/Pd TCs were constructed from Pd of 99.997% and 99.95% to 99.98% purity. The Pt wire was 99.999% pure. Stability tests are conducted at the Ag freezing point (962 °C) after an anneal or exposure test. Thus far, the optimal annealing temperature was found to be in the range 1300 °C to 1350 °C. Following annealing, eight of the TCs have been heated for 1000 hours at 1100 °C. Changes in emf corresponded to ≤ 0.1 °C, a repeatability 2-3 times better than standard high temperature TCs (types R, S, and B), with 80-85% of the change occurring during the first 350 hours. Tests for immersion characteristics at 962 °C after heat treatments at several other temperatures are in progress. The investigation of Pt/Pd TCs and a reference function for the range 0 °C to at least 1350 °C will be completed next year.

As part of our efforts in assisting industry to improve its thermometry, the stability of type K TCs containing special metal-sheath materials (two types) was compared with that of TCs with the usual Inconel sheaths. The evaluation involved heating the TCs in air for 1000 hours at 1260 °C. Compared with changes in calibration of 12 °C for the Inconel-sheathed TCs at this temperature, the special-sheathed TCs underwent changes of no more that 3 °C, i.e., changes at least four times smaller. Hence, by using the special-sheathed TCs, which now are available commercially, industrial users of type K TCs can improve the accuracy of their temperature measurements by a factor of at least four.

Some of our effort on new thermometric sensors involves evaluation of thin-film thermometers. An apparatus to provide accurate calibrations and evaluation of the stability of resistance heaters/thermometers on micro-hotplate devices at temperatures up to 600 °C was designed, constructed and evaluated. Microscopic radiometric measurements of temperature profiles on such micro-hotplate sensors were made in collaboration with the Semiconductor Electronics Division. After the stability of these sensors have been evaluated in FY95, they will be calibrated as thermometers for use in gas sensing studies.

C. Outputs and Interactions (Process Measurements Division)

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Zachariah, M.R. and Burgess, Jr., D.R.F., "Strategies for Laser-Excited Fluorescence Spectroscopic Measurements of Gas Phase Species During Particle Formation," J. Aerosol Science 25, 487-497 (1994).

Zachariah, M.R., Carrier, M.J., and Blaisten-Barojas, E., "Atomistic Simulation of Vapor-Phase Nanoparticle Formation," in Materials Research Society Proceedings, Molecularly-Designed Ultrafine/Nanostructural Materials 351, 343 (1994).

Zachariah, M.R., Carrier, M.J., and Blaisten-Barojas, E., "Molecular Dynamics Simulation of Large Cluster Growth," in Materials Research Society Proceedings, Gas-Phase and Surface Chemistry in Electronic Materials Processing 334, 75 (1994).

Zachariah, M.R. and Tsang, W., "Application of *Ab Initio* Molecular Orbital and Reaction Rate Theories to Nucleation Kinetics," Aerosol Science Technology 19, 499 (1993)

Zachariah, M.R. and Tsang, W., "Theoretical Calculation of Thermochemistry, Energetics and Kinetics of High Temperature $Si_xH_yO_z$ Reactions," J. of Physical Chemistry (in press).

Zachariah, M.R. and Tsang, W., "Theoretical Prediction of Gas-Phase Nucleation Kinetics of SiO," in Materials Research Society Proceedings, Gas-Phase and Surface Chemistry in Electronic Materials Processing 334, 19 (1994).

2. Talks

Amato Wierda, C., "Molecular Beam Mass Spectrometry in Materials Chemistry Problems: Chemical Vapor Deposition and Nanoparticle Synthesis," 12th Annual Meeting of Capital District Region, Kinetics and Dynamics Group, Albany, NY, January 29, 1994.

Burgess, Jr., D.R.F., "Chemistry of Fluorinated Species in Hydrocarbon Flames," NIST Annual Fire Conference, Rockville, MD, October 19, 1993.

Burgess, Jr., D.R.F., "Chemistry of Fluorinated Species in Hydrocarbon Flames," AIChE Annual Meeting, St. Louis, MO, November 9, 1993.

Burgess, Jr., D.R.F., "Reaction Pathways and Reduced Mechanisms Leading to Silicon Oxide Particle Formation," 1993 Fall Meeting of the Materials Research Society, Boston, MA, November 29, 1993.

Burgess, Jr., D.R.F., "Fluorinated Hydrocarbon Flame Suppression Chemistry," ACS, San Diego, CA, March 14, 1994.

Burgess, Jr., D.R.F., "Kinetics of Fluorine-Inhibited Hydrocarbon Flames," Halon Options Technical Working Conference, Albuquerque, NM, May 4, 1994.

Burgess, Jr., D.R.F., "Kinetics of Fluorine - Inhibited Hydrocarbon Flames," Halons Options Technical Working Conference, Albuquerque, NM, May 4, 1994.

Burgess, Jr., D.R.F., "Key Species and Important Reactions in Fluorinated Hydrocarbon Flame Chemistry: Premixed Flame Simulations and Measurements," ACS Annual Meeting, Washington DC, August 25, 1994. Invited

Burns, G.W., "Thermocouple Thermometry," Precision Thermometry Workshop, NIST, Gaithersburg, MD, October 21, 1993.

Burns, G.W., "The International Temperature Scale of 1990 (ITS-90)," Centro Nacional de Metrologia (CENAM), Querétaro, Mexico, November 2, 1993. Invited

Burns, G.W., "Thermocouple Thermometry," Centro Nacional de Metrologia (CENAM), Querétaro, Mexico, November 5, 1993. Invited

Burns, G.W., "Thermocouple Thermometry," Precision Thermometry Workshop, NIST, Gaithersburg, MD, March 24, 1994.

Cavicchi, R.E., "Micromachined Micro-hotplate Arrays for Efficient Processing of Materials," 40th National Symposium of the AVS, Orlando, FL, November 15, 1993.

Cavicchi, R.E., "Pulsed Desorption Kinetics Using Micromachined Micro-Hotplate Arrays," 40th National Symposium of the AVS, Orlando, FL, November 15, 1993.

Cavicchi, R.E., "Micro-hotplate Gas Sensor," Solid State Sensor and Actuator Workshop, Hilton Head, SC, June 13, 1994.

Cavicchi, R.E., "Micro-hotplate Temperature Control for Sensor Fabrication, Study, and Operation," 5th International Meeting on Chemical Sensors, Rome, Italy, July 14, 1994.

Cleveland, W.G., "High Accuracy Liquid Volumetric Measurement," Joint API/NIST Calibration Procedures Working Group Meeting, NIST, Gaithersburg, MD, May 16, 1994.

Collison, M.E., "Biosensor Design Strategies Based on Self-Assembly of Chemically Selective Interfaces," 184th Meeting of the Electrochemical Society, New Orleans, LA, October 14, 1993.

Collison, M.E., "Nanoscale Self-Organizing Biomolecular Arrays: Approaching the Next Generation of Biosensors and *in vitro* Diagnostics," Eli Lilly and Company, Indianapolis, IN, October 18, 1993.

Collison, M.E., "Immobilization of Enzymes at Biosensor Surfaces using Spontaneous Self-Assembly Phenomena," The Third World Congress on Biosensors, New Orleans, LA, June 1, 1994.

Collison, M.E., "Supramolecular Self-Assembly-Based Immobilization and Patterning of Biomolecules at Gold Electrode Surfaces," 208th American Chemical Society National Meeting, Washington, DC, August 29, 1994.

Davis, R.W., "Numerical Modeling of Heat Transfer in a Supercritical Water Pipe Flow," AIChE Annual Meeting, St. Louis, MO, November 9, 1993.

Gupta, A.K., "The Role of Combustion on the Transport of Droplets in Pressure-Atomized Spray Flames," 32nd AIAA Aerospace Sciences Meeting, Reno, NV, January 10, 1994.

Gupta, A.K., "Dispersion of Droplets in a Swirling Pressure-Atomized Spray Flame," 6th International Conference on Liquid Atomization and Spray Systems (ICLASS-94), Rouen, France, July 21, 1994.

Hodges, J.T., "Shear-Induced Motion in Suspended Droplets," 12th Annual Meeting of the American Association for Aerosol Research, Oak Brook, IL, October 12, 1993.

Hodges, J.T., "Internal Droplet Circulation Induced by Surface Driven Rotation," Technical Meeting, Central States Section of the Combustion Institute, Madison, WI, June 6, 1994.

Hodges, J.T., "Forward Scattering of a Gaussian Laser Beam by a Nonabsorbing Sphere," Scientific Conference on Obscuration and Aerosol Research, Edgewood Research, Development and Engineering Center, Dept. of the Army, Edgewood, MD, June 22, 1994.

Hodges, J.T., "Internal Droplet Circulation Induced by Surface Driven Rotation," Scientific Conference on Obscuration and Aerosol Research, Edgewood Research, Development and Engineering Center, Dept. of the Army, Edgewood, MD, June 23, 1994.

Hodges, J.T., "Analysis of Droplet Arrival Statistics in a Pressure-Atomized Spray Flame," 25th International Symposium on Combustion, Irvine, CA, August 3, 1994.

Hodges, J.T., "Internal Circulation in a Spinning Droplet," 25th International Symposium on Combustion, Irvine, CA, August 4, 1994.

Huang, P., "NIST Round Robin on ppm Humidity Standards," SEMICON EAST, Boston, MA, October 19, 1993.

Huang, P., "Sensor Calibration of a SAW Resonator for Absolute Humidity Measurements in Microelectronic Packages," 5th International Meeting on Chemical Sensors, Rome, Italy, July 11, 1994.

Huang, P., "Humidity Measurement and Standards at NIST," International Workshop on Humidity Measurements and Standards, Torino, Italy, July 18, 1994.

Hurst, W.S., "Current work with Optically Accessible Flow Cell for Hydrothermal Oxidation Studies," AIChE Annual Meeting, St. Louis, MO, November 9, 1993.

Hurst, W.S., "Raman Spectroscopic Measurements in a Supercritical Water Flow Reactor," Analytical Inorganic Research Division, NIST, Gaithersburg, MD, November 18, 1993.

Hurst, W.S., "Optical Cell Design: High Pressure and Temperature Absorption Measurements," Princeton Hypersonic Tunnel Workshop, Princeton University, Princeton, NJ, December 7, 1993. Invited

Kreider, K.G., "Thin-Film Friction and Wear Sensors for Continuous Bearing Monitoring," Office of Naval Research, Atlantic Beach, NC, November 16, 1993. Invited

Kreider, K.G., "High Temperature Silicide Thin-film Thermocouples," 1993 Fall Meeting of the Materials Research Society, Boston, MA, November 30, 1993.

Kreider, K.G., "Heat Transfer in Multilayer Packages using Thin-Film Thermocouples," 1993 Fall Meeting of the Materials Research Society, Boston, MA, November 30, 1993.

Kreider, K.G., "Laser Transformed SiC Thin Films," 1994 Spring Meeting of the Materials Research Society, San Francisco, CA, April 5, 1994.

Mangum, B.W., "Temperature Scales," Precision Thermometry Workshop, NIST, Gaithersburg, MD, October 18, 1993.

Mangum, B.W., "Introduction to Thermometry and to the Course on Thermometry," Centro Nacional de Metrologia (CENAM), Querétaro, Mexico, November 2, 1993. Invited

Mangum, B.W., "Liquid-in-Glass Thermometry," Centro Nacional de Metrologia (CENAM), Querétaro, Mexico, November 3, 1993. Invited

Mangum, B.W., "Thermistor Thermometry," Precision Thermometry Workshop, NIST, Gaithersburg, MD, March 23, 1994.

Mangum, B.W., "Liquid-in-Glass Thermometry," Precision Thermometry Workshop, NIST, Gaithersburg, MD, March 23, 1994.

Marquardt, E., "Design Optimization of Linear-Arm Flexure Bearings," 8th International Cryocooler Conference, Vail, CO, June 28, 1994.

Mattingly, G.E., "Elbow Effects on Pipe Flows and Selected Flow Meters," FLOMEKO'93, Seoul, Korea, October 26, 1993.

Mattingly, G.E., "Fluid Flow Metrology: Standards and Related Research at NIST," National Research Laboratory of Metrology, Tsukuba, Japan, November 1, 1993. Invited

Mattingly, G.E., "Fluid Flow Measurement at NIST: Standards and Related Research," Virginia Power Workshop, Hyatt Hotel, Richmond, VA, November 9, 1993. Invited

Mattingly, G.E., "Flow Measurement and Related Research at NIST," ISA, Kansas City, MO, November 16, 1993.

Mattingly, G.E., "Gas Flow Measurements Using Piston Prover Techniques," MKS Instruments, Inc., Andover, MA, December 21, 1993.

Mattingly, G.E., "Round Robin Measurement Programs: Test Methods and Data Analyses," ASMAP Workshop, NIST, Gaithersburg, MD, January 10, 1994.

Mattingly, G.E., "Fluid Flow Metrology at NIST," Advantek International, Inc., Secaucus, NJ, February 7, 1994. Invited

Mattingly, G.E., "Gas Flow Measurement Standards," Gas Dynamic Dilution Workshop, NIST, Gaithersburg, MD, February 22, 1994.

Mattingly, G.E., "Flow Meter Installation Effects Research at NIST," Advantek International, Inc., Secaucus, NJ, February 7, 1994.

Mattingly, G.E., "NIST Fluid Flow Measurement Standards, Capabilities, and Related Research," Colorado Engineering Experiment Station, Inc. (CEESI), Nunn, CO, February 24, 1994.

Mattingly, G.E., "Flow Measurements Using Turbine Meters," Colorado Engineering Experiment Station, Inc. (CEESI) Flow Course, Nunn, CO, February 24, 1994. Invited

Mattingly, G.E., "Flow Standards at NIST: An Update," ASME Flow Measurement Committee Meeting, March 10, 1994.

Mattingly, G.E., "Fluid Flow Metrology: Theories and Practice," Instrument Testing Association Workshop, Ramada Renaissance Hotel, Washington, DC, April 8, 1994. Invited

Mattingly, G.E., "Flow Measurement Short Course," ISA 40th International Instrumentation Symposium, Hyatt Regency Hotel, Baltimore, MD, May 2-3, 1994. Invited

Mattingly, G.E., "Flow Meter Installation Effects," Water & Wastewater Instrumentation Testing Association of North America, Flow Measurement Workshop, Newburgh, NY, May 17, 1994.

Mattingly, G.E., "Turbine Meter Calibrations Using Volumetric Techniques," Colorado Engineering Experiment Station, Inc. (CEESI) Flow Course, Nunn, CO, June 23, 1994. Invited

Meyer, C.W., "Vapor Pressure and Gas Thermometry," Precision Thermometry Workshop, NIST, Gaithersburg, MD, October 19, 1993.

Meyer, C.W., "Vapor Pressure and Gas Thermometry," Precision Thermometry Workshop, NIST, Gaithersburg, MD, March 22, 1994.

Ochel, H., "High-Pressure Raman-Spectroscopic *in situ* Observation of Intermediaries of Chemical Reactions in Hot Water," 12th Symposium on Thermophysical Properties, Boulder, CO, June 21, 1994.

Ochel, H., "Optical Probing of the Supercritical Water Environment," 12th International Conference on the Properties of Water and Steam, Orlando, FL, September 13, 1994.

Poirier, G.E., "Anisotropic Domain Growth and 1D Faceting in Self-Assembled Monolayers," Metallurgy Division Seminar, NIST, Gaithersburg, MD, November 10, 1993. Invited

Poirier, G.E., "Scanning Tunneling Microscopy of Pd Deposited on $Sn0_2$ Surfaces," 40th National Symposium of the AVS, Orlando, FL, November 16, 1993.

Poirier, G.E., "Scanning Tunneling Microscopy of Alkanethiol Self-Assembled Monolayers," NIST Surface Science Lunch Bunch, Gaithersburg, MD, November 29, 1993. Invited

Poirier, G.E., "The Structure and Ordering Dynamics of Alkanethiol Self-Assembled Monolayers on Au (111) Characterized by Scanning Tunneling Microscopy," Gordon Research Conference, Ventura, CA, February 28, 1994.

Poirer, G.E., "Phases of Alkanethiol Self-Assembled Monolayers on Au(111): The c(4x2), the px$\sqrt{3}$, and the 2-D Liquid Phase," Workshop on Industrial Applications of Scanned Probe Microscopy, NIST, Gaithersburg, MD, March 4, 1994.

Poirier, G.E., "Phases, Dynamics, and Defects in Alkanethiol Self-Assembled Monolayers on Au(111) Characterized by Scanning Tunneling Microscopy," Princeton University, Princeton, NJ, May 6, 1994. Invited

Presser, C., "Behavior of Droplets in Pressure-Atomized Spray Flames," 12th Annual Meeting of the American Association for Aerosol Research, Oak Brook, IL, October 12, 1993.

Presser, C., "Assessment of Halon Alternatives for Suppression of Turbulent Spray Flames," NIST Annual Conference on Fire Research, Rockville, MD, October 20, 1993.

Presser, C., "Assessment of Halon Alternatives for Suppression of Turbulent Spray Flames," AIChE Annual Meeting, St. Louis, MO, November 7, 1993.

Presser, C., "A Turbulent Spray Burner for Assessing Halon Alternative Fire Suppressants," ASME Winter Annual Meeting, New Orleans, LA, December 2, 1993.

Radebaugh, R., "Review of Pulse Tube Refrigeration," 8th International Cryocooler Conference, Vail, CO, June 28, 1994.

Ripple, D.C., "Overview of Radiation Thermometry," Precision Thermometry Workshop, NIST, Gaithersburg, MD, October 22, 1993.

Ripple, D.C., "Thermocouple Thermometry," Precision Thermometry Workshop, NIST, Gaithersburg, MD, March 24, 1994.

Ripple, D.C., "Overview of Radiation Thermometry," Precision Thermometry Workshop, NIST, Gaithersburg, MD, March 25, 1994.

Rosasco, G.J., "NIST Program in Support of Supercritical Water Oxidation," National Supercritical Water Oxidation Steering Program Committee Meeting, Washington, DC, December 2, 1993.

Rosasco, G.J., "Trends and Objectives: National Institute of Standards and Technology," 8th International Forum Process Analytical Chemistry, Montgomery, TX, January 24, 1994.

Rosasco, G.J., "Process Measurements Research in the Chemical Science and Technology Laboratory," Eli Lilly and Co., Indianapolis, IN, February 15, 1994.

Rosasco, G.J., "Computational Fluid Dynamics Research in the Process Measurements Division," Eli Lilly and Co., Indianapolis, IN, February 16, 1994.

Semancik, S., "Development of Gas Microsensor Arrays," Neural Net Workshop, University of Maryland, College Park, MD, November 4, 1993. Invited

Semancik, S., "Development of CMOS-Based Gas Microsensor Arrays with Materials and Kinetic Selectivity," 40th National Symposium of the AVS, Orlando, FL, November 18, 1993.

Semancik, S., "Development of CMOS-Based Microsensor Arrays for Analysis of Gas Mixtures," 8th International Forum on Process Analytical Chemistry, Houston, TX, January 24, 1994. Invited

Semancik, S., "Gas Microsensor Arrays: Active Oxide Surfaces on Micromachined Silicon," Texas A&M University, College Station, TX, January 27, 1994. Invited

Semancik, S., "Advanced Materials and Concepts for Solid State Gas Sensing," 1994 Spring Meeting of the American Physical Society, Pittsburgh, PA, March 24, 1994.

Semancik, S., "Development of Gas Microsensor Arrays: Combining Surface Chemistry with CMOS Technology," 21st Annual Michigan AVS Spring Symposium, Wayne State University, Detroit, MI, May 19, 1994. Invited

Semancik, S., "Developments in Solid State Gas Sensing Technology at NIST," Ford Motor Company, Research Laboratory, Dearborn, MI, June 9, 1994. Invited

Semancik, S., "Development of Microstructure-Controlled and Ultrathin SnO_2 Gas Sensing Films," 5th International Meeting on Chemical Sensors, Rome, Italy, July 14, 1994.

Semancik, S., "Research at NIST on SnO_2 Crystals, Films and Conductometric Microsensor Arrays," University of Brescia, Brescia, Italy, July 19, 1994. Invited

Semancik, S., "Surface Science and the Development of Gas Microsensor Arrays," Cornell University, Ithaca, NY, September 8, 1994. Invited

Siegwarth, J.D., "Liquid Hydrogen Work/Flowmeters," Space Instrumentation Workshop, Huntsville, AL, February 16, 1994.

Sobolewski, M.A., "Sensitivity of Argon Plasmas to O_2, N_2, and H_20 Impurities," 46th Annual Gaseous Electronics Conference, Montreal, Canada, October 19, 1993.

Sobolewski, M.A., "Electrical Measurements for Monitoring and Control of Radio-Frequency Plasmas," SEMATECH, Austin, TX, December 2, 1993.

Sobolewski, M.A., "Measuring and Analyzing the Electrical Characteristics of Radio-Frequency Glow-Discharges," Lawrence Livermore National Laboratory, Livermore, CA, May 20, 1994.

Sobolewski, M.A., "Electrical Measurements for Monitoring and Control of Radio-Frequency Plasmas," SEMATECH, Austin, TX, August 24, 1994.

Strouse, G.F., "Platinum Resistance Thermometry," Precision Thermometry Workshop, NIST, Gaithersburg, MD, October 18, 1993.

Strouse, G.F., "Uncertainties of Measurements," Centro Nacional de Metrologia (CENAM), Querétaro, Mexico, November 3, 1993. Invited

Strouse, G.F., "Resistance Thermometry," Centro Nacional de Metrologia (CENAM), Querétaro, Mexico, November 4, 1993. Invited

Strouse, G.F., "Platinum Resistance Thermometry," Precision Thermometry Workshop, NIST, Gaithersburg, MD, March 21, 1994.

Tarlov, M.J., "Photopatterning of Alkanethiol Monolayers Self-Assembled on Gold and Silver," Pennsylvania State University, University Park, PA, November 3, 1993. Invited

Tarlov, M.J., "UV Photopatterning of Alkylthiolate Monolayers Self-Assembled on Gold," 40th National Symposium of the AVS, Orlando, FL, November 17, 1993.

Tarlov, M.J., "UV Photopatterning of Alkanethiol Monolayers on Gold and Silver," 1993 Fall Meeting of the Materials Research Society, Boston, MA, December 2, 1993.

Tarlov, M.J., "UV-Photopatterning of Alkanethiol Self-Assembled Monolayer," Gordon Research Conference on Organic Thin Films, Ventura, CA, March 3, 1994.

Tarlov, M.J., "Photopatterning of Alkylthiol Self-Assembled Monolayers," ACS Annual Meeting, Denver, CO, March 20, 1994.

Tarlov, M.J., "The Structure and Ordering Dynamics of Alkanethiol Self-Assembled Monolayers on Au(111)," Max Planck Institute for Polymer Research, Mainz, Germany, March 24, 1994.

Tarlov, M.J., "Controlling the Position of Biomolecules on Surfaces with Photopatterned Self-Assembled Monolayers," 30th Annual New Mexico AVS Symposium, Albuquerque, NM, April 20, 1994. Invited

Tarlov, M.J., "Controlling the Position of Biomolecules on Surfaces with Photopatterned Alkanethiol Monolayers," Los Alamos National Laboratory, Los Alamos, NM, April 22, 1994.

Tarlov, M.J., "Controlling the Position of Biomolecules on Surfaces with Photopatterned Alkanethiol Monolayers," Department of Chemistry, University of Wyoming, Laramie, WY, April 27, 1994. Invited

Tarlov, M.J., "Self-Assembled Monolayers," Maryland State Governor's Academy Workshop, NIST, Gaithersburg, MD, July 12, 1994.

Tarlov, M.J., "Surface Plasmon Microscopy of Biomolecular Recognition Reactions on UV-Photopatterned Alkanethiol Self-Assembled Monolayers," ACS 208th National Meeting, Washington, DC, August 25, 1994.

Tarlov, M.J., "Phases, Dynamics and Defects in Alkanethiol Self-Assembled Monolayers," ACS 208th National Meeting, Washington, DC, August 29, 1994.

Tew, W.L., "High Accuracy Calibrations of Resistance Thermometers at NIST on the ITS-90," NASA Goddard/Earth Observer Satellite Calibration Panel, Rockville, MD, March 1, 1994. Invited

Tew, W.L., "Temperature Scales," Precision Thermometry Workshop, NIST, Gaithersburg, MD, March 21, 1994.

Tew, W.L., "Low Temperature Calibrations," Precision Thermometry Workshop, NIST, Gaithersburg, MD, March 22, 1994.

Westmoreland, P.R., "Kinetics of Fluoromethanes in Flames," Combustion Institute/Eastern States Section Fall Technical Meeting, Princeton, NJ, October 27, 1993.

Westmoreland, P.R., "Fluoromethane Chemistry and Its Role in Flame Suppression," 25th International Symposium on Combustion, Irvine, CA, August 2, 1994.

Whetstone, J.R., "Navy Humidity Generator Certification Program using the NIST Primary Standard Gravimetric Hygrometer," National Conference of Standards Laboratories, 1994 Workshop and Symposium, Chicago, IL, August 2, 1994.

Whetstone, J.R., "Solid State Sensing Technology Development," EPA Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, August 9, 1994.

Zachariah, M.R., "Molecular Dynamics Simulation of Large Cluster Growth," AIChE Annual Meeting, St. Louis, MO, November 11, 1993.

Zachariah, M.R., "Application of *Ab initio* Molecular Orbital and Reaction Rate Theories to Gas-Phase Nucleation Kinetics," AIChE Annual Meeting, St. Louis, MO, November 11, 1993.

Zachariah, M.R., "Theoretical Prediction of Gas-Phase Nucleation Kinetics for SiO," 1993 Fall Meeting of the Materials Research Society, Boston, MA, November 29, 1993.

Zachariah, M.R., "Molecular Dynamics Simulation of Large Silicon Cluster Growth," 1993 Fall Meeting of the Materials Research Society, Boston, MA, November 29, 1993.

Zachariah, M.R., "Formation of Superparamagnetic Nanocomposites from Vapor Phase Condensation in a Flame," 1994 Spring Meeting of the Materials Research Society, San Francisco, CA, April 6, 1994.

Zachariah, M.R., "Atomistic Simulation of Vapor-Phase Nanoparticle Formation," 1994 Spring Meeting of the Materials Research Society, San Francisco, CA, April 7, 1994.

Zachariah, M.R., "Vapor Phase Combustion Synthesis of Nanostructured Materials," Yale University, New Haven, CT, May 2, 1994. Invited

Zachariah, M.R., "Application of Computational Chemistry Methods to Some Problems in Chemical Engineering," Yale University, New Haven, CT, May 4, 1994. Invited

Zachariah, M.R., "Theoretical Prediction of Thermochemistry and Kinetics of Fluorocarbons," ACS Annual Meeting, Washington, DC, August 25, 1994. Invited

3. Cooperative Research and Development Agreements (CRADAs) and Consortia

Processing of Ceramic Powders, M.R. Zachariah
NanoPhase Technologies (CRADA)

Chemical Measurements for Power Plants, W. Hurst
Babcock & Wilcox Company (CRADA)

Filter Materials Accelerated Life Testing, S.R. Charagundla and A. Maček
Pall Corporation (CRADA)

On-line Spectroscopy of Various Metalorganics used in Compound Semi Conductors, S.R. Charagundla
Morton International/CVD Metalorganics (CRADA)

Thermal Processes and Hazardous Waste Destruction, C. Presser and J.T. Hodges
Scientific Applications International Corporation (CRADA)

Combustion of Acoustically Driven Atomized Sprays, C. Presser
Fluid Jet Associates (CRADA)

Solder Jet Science and Technology, C. Presser
Microfab Technologies (CRADA)

Development of 400 Hz OPTR, R. Radebaugh
Tektronix (CRADA)

Pressure Oscillators for Cryocoolers, R. Radebaugh
Clovis Thermal (CRADA)

Pulse Tube Refrigerator Test Facility, R. Radebaugh
Hughes Aircraft (CRADA)

Cryogenic Catheter, R. Radebaugh
Aegis Medical Technologies (CRADA)

TADOPTR for Gas Liquefaction, R. Radebaugh
Cryenco Sciences (CRADA)

Flowmeter Installation Effects Consortium, G.E. Mattingly
- British Columbia Hydro & Power Authority
- Chevron Oil Field Research Company
- Consolidated Edison
- Controlotron, Inc.
- Dow Chemical U.S.A.
- E.I. DuPont de Nemours & Company
- Fisher Precision Systems, Inc.
- Ford Motor Company
- Ketema - McCrometer Division
- Ketema - Schutte & Koerting Division
- Kimmon Manufacturing Company, Ltd. (Japan)
- N.V. Nederlands Gasunie
- NRTC (NOVACOR Research Technology Corporation)
- Pacific Gas & Electric Company

4. Patent Awards and Applications

Kreider, K.G., "Corrosion Resistant Thin Film Thermocouples and Method," Patent No. 5,251,981 (issued October 1993)

Kreider, K.G., "Process for Transparent Carbon Nitride Coating," (submitted February 1994)

Semancik, S. and Cavicchi, R.E., "Planar Epitaxial Films of SnO_2," Patent No. 5,330,855 (issued July 1994)

Semancik, S., Cavicchi, R.E., and Gaitan, M., "Temperature-Controlled, Micromachined Arrays for Chemical Sensor Fabrication and Operation," Patent No. 5,345,213 (issued September 1994)

Tarlov, M.J., "Process for UV-Photopatterning of Thiolate Monolayers Self-Assembled on Gold, Silver and Other Substrates," (filed April 1994)

5. SRM Activities

SRM 1744	Aluminum Freezing-Point Standard (completed)

6. SRD Activities

SRD 45	GRI/NIST Orifice Meter Discharge Coefficient (new)
SRD 60	ITS-90 Thermocouple Database (new)

7. **Calibrations**

Calibration services have been provided for the following:

ABB C-E Services Inc.
Abbott Labs
Accuracy Scientific Inst.
Aerospace Process Technology
Air Products & Chemicals Inc.
Airflow Technical Products Inc.
Allegheny Power System
Allied Signal Aerospace
Aluminum Co of America
American Meter Co.
American Red Cross
Ametek Aersospace Products
Amoco Oil
Analytical Technologies Inc.
Aphis-Animal Damage Control
ARI Industries Inc.
Arizona Public Service Co.
AT&T
AVX Corp.
Babcock & Wilcox
Baltimore Gas & Electric Co.
Barber Colman Co.
Barnant Co.
Baxter Healthcare Corp.
Becton Dickinson & Co.
Brooklyn Thermometer Co Inc.
Brooks Instruments
Buckeye Pipe Line Co.
C & M International Inc.
C-Temp
Carmel Forge Ltd.
Centerior Energy
Centerior Service Co.
CGS Thermodynamics
CI Systems Ltd.
City of Rockville
Cleveland Electric Labs
Climatronics Corp.
Coca Cola Bottling Co.
Commonwealth Edison Co.
Comtel Instruments Co.
Conrad Kacsik Inst Sys Inc.
Consumers Power Co.
Convectronics Inc.
Coors Brewing Co.
Corning Inc.
County of Los Angeles
Cozad Instrument Co.
Cummins Engine Co. Inc.
Detroit Edison
DHHS/FDA
Douglas Aircraft Co.
Dow Corning Corp.
Dry Dock Co.
Duke Power Co.
Duro Sense Corp.
E-Systems Inc.
E2 Technology Corp.
Eastern Stainless Corp.
Eastman Kodak Co.
EG&G Idaho Inc.
EG&G Inc.
EG&G Mound Applied Tech.
EG&G Rotron Inc.
EI Dupont De Nemours & Co. Inc.
Eli Lilly & Co.
Engelhard Corp.
Engelhard West Inc.
Environmental Systems Corp.
Ertco Inc.
Ever Ready Thermometer Co Inc.
Exxon Co USA
Finnish Meterorological Inst.
Fisher Scientific Co.
FLW Service Corp.
Furnace Parts Inc.
Gayesco
General Eastern Instruments
General Electric Co.
General Motors Corp.
Geomet Technologies Inc.
Georgia Dept. of Agriculture
Grumman Aerospace Corp.
GTE California

Hart Scientific
Heraeus Sensor
Hill Top Biolabs Inc.
Hoffer Flow Controls Inc.
Hoffmann-La Roche Inc.
Hoskins Mfg. Co.
Houston Lighting and Power Co.
Howmet Corp.
Hutchinson Technology Inc.
ICL Calibration Labs Inc.
Idaho Labs Corp.
Illinois Power Co.
Inco Alloys International Inc.
Industronics Service Co.
Instrulab Inc.
Instrument Lab.
Intech Automation Sys Corp.
Jet Propulsion Lab
JMS Southeast Inc.
Johnson Controls World Svcs.
Johnson Gage & Inspection Inc.
Johnson Matthey
Joliet Metallurgical Labs Inc.
Kaman Aerospace Corp.
Kaye Instruments Inc.
Kayness Inc.
Kennametal Inc.
Ketema
Klock
Kulas Systems Inc.
Kurz Instruments Inc.
Lab Tecnologico Del Uruguay
Ladish Co. Inc.
Lake Shore Cryotronics Inc.
Linco Electromatic Inc.
Lockheed advanced Development
Lockheed Ft. Worth Co.
Lockheed Missiles & Space Co.
Loy Instrument Inc.
LS Starrett Co.
Magnavox Electronic Systems Co.
Maimonides Medical Center
Mallinckrodt Chemical Inc.
Marine Corps Logistics Base
Marlin Mfg. Corp.
Martin Marietta Astronautics
Martin Marietta Corp.
Martin Marietta Specialty Com.
McDonnell Douglas Corp.
McDonnell Douglas Tulsa
McGill Mfg. Co. Inc.
McNeil Pharmaceutical
MCS Calibration Inc.
MD Instruments Inc.
Medi-Flex Hospital Products
Melcam Standards Lab
Meter Engineers Inc.
Micron Intruments
Mid America Pipeline Co.
Miller & Weber Inc.
MKS Instruments Inc.
Modern Instrument Co. Inc.
Montana Power Co.
Montgomery County Gov't
MVM Entrerprisers
NASA Goddard Space Flight Ctr.
NASA Langley Research Ctr
National Basic Sensor
National Standards of Puerto Rico
Naval Air Warfare Center
Naval Aviation Depot
Naval Weapons Station
Nelson Instrument
Nelson Jameson Inc.
Newark AFB
Niantic Envirolab Inc.
Northrop Corp.
Nutrasweet Co.
Omega Engineering Inc.
Owens-Corning Metal Facility
Paramax Systems Corp.
Pemberton Fabricators Inc.
Pemco Aeroplex Inc.
PGP Industries Inc.
Philadelphia Electric Co.
Philips Semiconductors
Phys-Chem Scientific Corp.
Plantation Pipe Line Corp.
PMC Corp.
Pratt & Whitney
Projects Inc.
Pyco Inc.

Pyromation Inc.
Pyrometric Service Co
R P Services
RAM Sensors
Raytheon Co.
Recra Environmental Inc.
Response Technologies Inc.
Rockwell International
Rolock of California Inc.
Rome Laboratory
Rosemount Inc.
Ruska Instrument Corp.
Sandia National Labs
Sanofi Diagnostics Pasteur Inc.
Santa Barbara Infrared Inc.
Santee Cooper
Sensor Scientific Inc.
Service Associated Inc.
SGS-Thomson Microelectronics
Sherwood Medical
Smith Meter Inc.
Smithkline Beecham
Solomat/Neotronics Co.
Southwestern Public Service Co.
Special Metals Corp.
Sper Scientific Ltd.
St. Paul Medical Center
Stabro Labs Inc.
State of Arizona
Stillings Instrument Systems
Systec Inc.
Tacoma Pierce City Blood Bank
Temp-Pro Inc.
Teradyne Inc.
Testoterm Inc.
Texas Instruments
Thermacal Inc.
Thermo Electric
Thermo-Temp Instruments Inc.
Thermogage Inc.
Transmation Inc.
TRC Environmental Corp.
TRW Space & Defense Sector
TRW Space & Electronics Group
TU Electric
US Army Dugway Proving Ground
US Army Research Lab
US Army TMDE Activity
US Department of Commerce
US Department of Labor
Vaisala Inc.
Valley Heat Treat Co.
Velcro
Voix Corp.
Wash Pub Pwr Supp System
Watlow Gordon
Weed Instrument Co. Inc.
Westinghouse Electric Corp.
Westinghouse Hanford Co.
Westinghouse Savannah River Co.
Williams Pipe Line Co.
Wyeth Ayerst Labs
Wyman-Gordon Forging
YSI Inc.

8. Committee Assignments

D.R.F. Burgess, Jr.

NIST/SEMATECH Chemical Kinetics Data Base Steering Committee
NIST Advanced Technology Laboratory Technical Advisory Group

G.W. Burns

ASTM E-20 Committee on Temperature Measurement
ASTM Subcommittee E-20.04, Thermocouples
ASTM Subcommittee E-20.90, Executive Subcommittee
Instrument Society of American SP-1.1, Committee on Temperature Measurement (Thermocouples)

W.G. Cleveland

ASHRAE Technical Committee 1.2, Instruments and Measurements

J.F. Houser

ASTM Subcommittee E-20.05, Liquid-in-Glass Thermometers and Hydrometers

P. Huang

ASHRAE Committee, Standard Methods for Measurement of Moist Air Properties
Working Group on Hygrometry, International Committee on Weight and Measures (Chair)

M.J.G. Kaeser

ASTM E-20 Committee on Temperature Measurement
ASTM E-20.04, Thermocouples
ASTM E-20.06 New Thermometers and Techniques

K.G. Kreider

ASTM E20 Committee on Temperature Measurement
ASTM E20.04 Subcommittee on Thermocouples
IEEE Technical Committee on Sensor Standards, TC-9 (Chairman)

A. Lee

Environmental Technologies Working Group, Dept. of Commerce
Joint Subcommittee on Environmenal Technologies, Committee on Envrironmental and Natural Resources, National Science and Technology Council
Pollution Prevention Committee, Environmental Technology Initiative, Environmental Protection Agency (EPA)
Environmenal Technologies Committee, Environmental Technology Initiative, Environmental Protection Agency (EPA)
Manufacturing Extension Partnership (MEP) Working Group, NIST

A. Maček

Combustion Institute - 25th Symposium (International) on Combustion, Program Subcommittee
AIChE Area 3B Committee on Fluidization and Fluid Particle Systems
Combustion Reaction Engineering, AIChE Annual Conference (Co-Chairman)

B.W. Mangum

ASTM E-20 Committee on Temperature Measurement (Chairman, 1994)
ASTM Subcommittee E-20.03, Resistance Thermometers
ASTM Subcommittee E20.06, New Thermometers and Techniques (Chairman)
ASTM Subcommittee E-20.07, Fundamentals in Thermometry
ASTM Subcommittee E-20.08, Medical Thermometry
  Working Group WG.02, Fever Thermometers
  Working Group WG.02A, Electronic Fever Thermometers
  Working Group WG.02C, Disposable Fever Thermometers
  Working Group WG.03, Continuous Clinical Temperature Monitoring Systems
  Working Group WG.04, Clinical Laboratory Temperature Measurement
ASTM Subcommittee E-20.90, Executive Subcommittee (Chairman, 1994)
Comité Consultatif de Thermométrie (of the CIPM, Delegate)
Working Group 1, Defining Fixed Points and Interpolating Instruments (Chairman)
International Electrotechnical Commission, (IEC) TC65/SC65B/WG5, Industrial Process Measurement and Control/Devices/Temperature Sensors (Chairman of WG5)

G.E. Mattingly

ASME Main Committee on the Measurement of Fluid Flow in Closed Conduits
ASME SC-2 Subcommittee on Pressure Differential Devices
ASME SC-6 Subcommittee on Glossary of Terms for Flow Measurements
ASME SC-14 Subcommittee on Measurement of Fluid Flow Using Gravimetric and Volumetric Techniques (Chairman)
ASME SC-15 Subcommittee on Installation Effects on Flowmeters
ASME SC-16 Subcommittee on Vortex Shedding Type Flowmeters
ASME Main Research Committee on Fluid Meters
ASME SC-11 Subcommittee on Test Methods and Calculation Procedures (Chairman)
International District Heating Association: Testing Heat Meters Used in Fluid HVAC Systems
International Measurement Congress (IMEKO) Technical Committee No. 9 - Flow Measurement
Technical Advisory Committee for the GRI Sponsored Flow Metering Research Program at Southwest Research Institute

C. Presser

ASME K6-Committee on Heat Transfer in Energy Systems
Combustion Institute - 25th Symposium (International) on Combustion, Program Review Subcommittee
ASTM Subcommittee E29.03 on Int'l Cooperation on Terminology, Standards and Methods of Particle Size Measurements
ASTM Subcommittee E29.04 on Liquid Particle Measurements, Committee E29 on Particle Size Measurements
ASTM Subcommittee E29.05 on Reference Materials, Committee E29 on Particle Size Measurements (Chairman)
AIAA National Energy Terrestrial Systems Technical Committee
ASME 1993 International Joint Power Generation Conference, Modeling of Combustion Systems (Co-chairman)
ASME 1994 Winter Annual Meeting, Heat Transfer in Hazardous Waste Processing (Co-chairman)
ASME 1994 International Joint Power Generation Conf., Pollutant Emission and Combustion Modeling, and Particle Transport and Combustion Phenomena (Co-chairman)
ASME 1993 Winter Annual Meeting, Symposium on Fluid Mechanics and Heat Transfer in Sprays, Heat and Mass Transfer in Spray Combustion Systems (Co-chairman)

R. Radebaugh

8th International Cryocooler Conference Advisory Committee (Member)
8th International Cryocooler Conference Local Arrangements (Chairman)
International Cryocooler Conference, Recording Secretary

D.C. Ripple

Comité Consultatif de Thermométrie (of the CIPM)
    Working Group 3, International Traceability in Temperature Measurements

G.J. Rosasco

NIST Human Research Ethics Committee
Scientific Board, 9th International Forum on Process Analytical Chemistry
Peer Review Panel, Accelerated Tri-Services Site Characterization and Analysis Penetrometer System (SCAPS) Sensor Development Project
Technical Advisory Committee (TAC) for the Army Research Office University Research Initiative on Thermal Treatment of Chemical Wastes

J.L. Scott

Technical Advisory Committee (TAC) for the GRI Metering Research Facility (MRF) at Southwest Research Institute (SwRI)
Transmission Measurement Committee of the American Gas Association (AGA)
North American AD Hoc Orifice Meter Expert Committee

S. Semancik

American Vacuum Society, Thin Film Division, Program Committee

C.D. Vaughn

ASTM Subcommittee E-20.05, Liquid-in-Glass Thermometers and Hydrometers

J.R. Whetstone

ISA Standards and Practices, Board of Directors

J.A. Wise

ASTM E-20 Committee on Temperature Measurement (Chairman in 1993)
ASTM Subcommittee E-20.05, Liquid-in-Glass Thermometers and Hydrometers (Secretary in first half of FY94)
ASTM Subcommittee E-20.90, Executive Subcommittee (Chairman in 1993)
ASTM Subcommittee E-20.91, Editorial and Nomenclature (Secretary in first half of FY94)

M.R. Zachariah

Combustion Institute - 25th Symposium (International) on Combustion, Program Subcommittee
AAAR Aerosol Technology Group (Chairman)
AIChE Material Engineering & Science, Area 8d. - Ceramics
NIST Focus Group on Industrial Application of Computational Chemistry
NIST/SEMATECH Chemical Kinetics Data Base Steering Committee

9. <u>Editorships</u>

G.E. Mattingly

International Journal of Flow Measurement and Instrumentation (North American Editor)

D.A. Olson

CSTL Update Newsletter (Editor)

C. Presser

Proc. Combustion Modeling, Scaling and Air Toxins, FACT-Vol. 18, Amer. Soc. Mech. Engr., NY, 1994
Proc. Fluid Mechanics and Heat Transfer in Sprays, FED-Vol. 178, HTD-Vol. 270, Amer. Soc. Mech. Engr., NY, 1994
Proc. Combustion Modeling, Cofiring, and NOx Control, FACT-Vol. 17, Amer. Soc. Mech. Engr., NY, 1993

R. Radebaugh

American Institute of Physics, Editor-in-Chief for book series "Modern Instrumentation and Measurements in Physics and Engineering"
Cryogenics (Advisory Editor)

10. Seminars

October 21, 1993

Dr. Ray Adomaitis, University of Maryland, College Park, MD, "Compressor Stall Control: A Case Study in Fluid Flow Stabilization." (Division Sponsor: D. Olson)

November 5, 1993

Kevin Carabell, The College of Engineering, University of Wisconsin, Madison, WI, "Air/Fuel Ratio Visualization in a Diesel Spray." (Division Sponsor: J.T. Hodges)

November 17, 1993

Prof. Edward A. Whittaker, Stevens Institute of Technology, Hoboken, NJ, "Diode Laser Absorption Spectroscopy for Sensitive Gas Phase Chemical Detection." (Division Sponsor: J.R. Whetstone)

November 18, 1993

Raymond D. Mountain, NIST, Thermophysics Division, Gaithersburg, MD, "Molecular Dynamics Simulation of Nonequilibrium Processes - A Cautionary Tale." (Division Sponsor: M.R. Zachariah)

November 23, 1993

Kristen Steffens, Molecular Physics Laboratory, Menlo Park, CA, "Vibrational Energy Transfer Effects on OH Detection in Flames using Predissociative LIF." (Division Sponsor: M.R. Zachariah)

December 1, 1993

Prof. William J. Devenport, Virginia Polytechnic Institute and State Univ., Blacksburg, VA, "Diode-Array Velocimetry and Prospective Applications to Fluid Flow Measurements." (Division Sponsor: G.E. Mattingly)

December 7, 1993

Drs. G. Gouesbet and G. Grehan, Laboratoire d'Energetique des Systemes et Procedes, Mont-Sant-Aignan, France, "Latest Developments in the Generalizaed Lorenz-Mie Theory." (Division Sponsor: J.T. Hodges)

December 22, 1993

Prof. B.M. Smirnov, Russian Academy of Sciences, Moscow, Russia, "Plasma Processes in Expanding and Condensing Gases." (Division Sponsor: J.T. Hodges)

January 13, 1994

Keith Carron, University of Wyoming, Laramie, WY, "Advanced Environmental Monitoring with Surface Enhanced Raman Probes." (Division Sponsor: M.J. Tarlov)

February 10, 1994

Prof. E. James Davis, University of Washington, Seattle, WA, "Recent Developments in Microparticle Raman Spectroscopy Using Electrodynamic Levitation." (Division Sponsor: J.T. Hodges)

March 2, 1994

Dr. Bruce T. Murray, NIST, Computing & Applied Mathematics Laboratory, Gaithersburg, MD, "Computational Fluids and Heat Transfer Using FIDAP." (Division Sponsor: M.R. Zachariah)

March 10, 1994

Bharat Soni and Pasquale Cinnella, Mississippi State University, Mississippi, MS, "Computational Field Simulation for Complex Physics/Complex Geometry." (Division Sponsor: R. Davis)

April 22, 1994

Dr. Allessandro Gomez, Yale University, New Haven, CT, "Combustion Applications of the Electrospray." (Division Sponsor: M.R. Zachariah)

May 4, 1994

Prof. Dawn A. Bonnell, The University of Pennsylvania, Philadelphia, PA, "Structure and Reactivity of Transition Metal Oxide Surfaces: ZnO, $SrTiO_3$, TiO_2." (Division Sponsor: S. Semancik)

May 6, 1994

Dr. Ilan Chabay, The New Curiosity Shop, Mountain View, CA, "Ping Pong Pinball^{TM}, Flowcomotion^{TM}, and The Crystal Spider^{TM}: New Technology and New Strategies for Communicating Science in Museums, Schools, Public Spaces, Corporations, and Courtrooms." (Division Sponsor: G.J. Rosasco)

May 11, 1994

Prof. Lynn A. Melton, University of Texas at Dallas, Richardson, TX, "Fluorescent Diagnostics for Droplets, Sprays and Combustion." (Division Sponsor: A. Maček)

May 12, 1994

Dr. George E. Keller II, Union Carbide Corporation, South Charleston, WV, "The Impact of New Chemical and Polymer Manufacturing Strategies on Needs for Process-Design and Process-Control Research." (Division Sponsor: G. Rosasco)

June 15, 1994

James G. Seebold, Chevron Research and Technology Company, Richmond, CA, "What is the Petroleum Environmental Research Forum (PERF Project No. 92-19) on Toxic Combustion Byproducts?" (Division Sponsor: C. Presser)

June 15, 1994

Prof. Peter Eisenberger, Princeton University, Princeton, NJ, "Self-Assembled Monolayers: Structure, Phases, and Growth." (Division Sponsor: G. Poirier)

June 29, 1994

Thomas A. Milne, National Renewable Energy Laboratory (NREL), Golden, CO, "History, Phenomena and Applications of Free-Jet, Molecular Beam Sampling." (Division Sponsor: C. Amato-Wierda)

July 6, 1994

Prof. Rosina M. Georgiadis, George Washington University, Washington, DC, "Electronic Structure at Solid/Liquid Interfaces by Nonlinear Optical Spectroscopy." (Division Sponsor: M.J. Tarlov)

July 20, 1994

Prof. S.K. Aggarwal, University of Illinois at Chicago, Chicago, IL, "Droplet-Vortex Interactions in Two-Phase Shear Flows." (Division Sponsor: C. Presser)

July 22, 1994

Michael T. Klein, University of Delaware, Newark, DE, "Reactions and Kinetics in Supercritical Fluids." (Division Sponsor: W. Hurst)

August 3, 1994

Dr. Don Rej, Los Alamos National Laboratory, Los Alamos, NM, "Plasma Processing at Los Alamos." (Division Sponsor: G.J. Rosasco)

August 3, 1994

Frank DiMeo, Jr., Northwestern University, Evanston, IL, "The Growth and Characterization of Bi-Sr-Ca-Cu-O Superconducting Thin Films Deposited by Metalorganic Chemical Vapor Deposition (MOCVD)." (Division Sponsor: S. Semancik)

August 26, 1994

Prof. Edmond F. Bowden, North Carolina State University, Raleigh, NC, "Protein Monolayer Electrochemistry: Electron Transfer in Cytochrome c/Alkanethiolate/Gold Structures." (Division Sponsor: M.J. Tarlov)

September 7, 1994

Prof. J.B. Joshi, University of Bombay, India, "Problem Areas in Multiphase Systems which Need Research Attention." (Division Sponsor: P.J. Giarratano)

11. Conferences/Workshops/Sessions Sponsored/co-Sponsored

October 4, 1993
Flow Meter Installation Effects Consortium Meeting, Gaithersburg, MD (G.E. Mattingly)

October 18-23, 1993
Precision Thermometry Workshop, Gaithersburg, MD (B.W. Mangum)

December 20, 1993
CVD Thermochemistry Meeting, Gaithersburg, MD (J.R. Whetstone)

January 10, 1994
Air Speed Measurement Assurance Program, Gaithersburg, MD (W.G. Cleveland)

March 21-25, 1994
Precision Thermometry Workshop, Gaithersburg, MD (B.W. Mangum)

June 7, 1994
Process Chemical Sensing Forum, Gaithersburg, MD (J.R. Whetstone)

July 27, 1994
NIST Flow Measurement Workshop: Flow Meter Users Perspectives, Gaithersburg, MD (G.E. Mattingly)

August 8, 1994
NIST Flow Measurement Workshop: Flow Meter Manufacturer Perspectives, Gaithersburg, MD (G.E. Mattingly)

August 23-24, 1994
Technical Opportunities and Research Needs for Fluid Processes and Properties Utilized in Process Design and Simulation, Boulder, CO (P.J Giarratano)

September 19, 1994
Process Chemical Sensor Forum Organizing Committee Meeting, Gaithersburg, MD (J.R. Whetstone)

VI. Surface and Microanalysis Science Division (837)

Rance A. Velapoldi, Chief

A. Division Overview

The Surface and Microanalysis Science Division conducts research and development to: (a) determine the chemistry and physics of surfaces, interfaces, particles, and materials, and their interactions with a broad spectrum of species including electrons, photons, ions, atoms, and molecules; (b) determine the chemical and isotopic composition and electronic structure of surfaces, particles, and materials down to nanometer spatial scales; (c) determine the energetics, kinetics, mechanisms, and effects of processes occurring on solid surfaces as well as within materials (or devices); (d) use chemometrics to study the total chemical measurement process and source apportionment in atmospheric chemistry, 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 bases for advances in various technologies, such as chemical catalysis, advanced electronics, and materials science.

This year Dale E. Newbury, Cedric J. Powell, and Lloyd A. Currie were selected by the Executive Review Board to become NIST Fellows based on their major research contributions with impact on science and technology at national and international levels. These scientific honors have major impact on our organizational structure. Fellows focus on research and will thus have more time to expand already exceptionally strong research interactions with NIST, national, and international programs in their areas of expertise. The Microanalysis Research Group, previously headed by Dale Newbury, was split into the Microanalysis Research and Analytical Microscopy Groups, headed by Eric B. Steel and David S. Simons, respectively. Staff members from Cedric Powell's Group were placed in the newly formed or existing Groups to provide similar or complementary functions. With these changes, the Surface and Microanalysis Science Division is well-positioned to contribute to the advanced measurement needs represented in the Laboratory's strategic thrusts of Biotechnology, Process Technology, Environmental Technologies, Fundamental Measurement Technology, and Health Care Technology.

In support of these thrusts, we proposed a major budget initiative to develop a "National Facility for Chemical and Materials Microanalysis". The proposed Facility would focus mainly on chemical sample characterization and investigation of surface interactions. Our unique capabilities in microprobe measurement science, developed over the last 20 years with a combination of Other Agency and Competence funds, allow us to provide state-of-the-art quantitative measurements at high spatial and temporal resolutions for fundamental measurement infrastructure and for the existing and emerging industrial technologies. Our approach expands and focuses our efforts in performing measurement research to develop the next generation tools and techniques to push the measurement envelope (*enabling technology*) and, through collaborative research, to apply these new measurement tools internally to NIST programs and externally to industrial and other government agency needs. The proposal was presented to NIST management and research staff and was a triggering event for a Nanotechnology Workshop, part of a NIST series of workshops held in September for management to establish new directions for initiatives. The importance of chemical characterization of a broad spectrum of materials and electronic devices at the nanometer scale at ultralow species concentrations was underscored at the Workshop. We will continue presenting the concept to various industries this year.

A significant part of our research in measurement science involves the development and use of state-of-the-art techniques to characterize chemical systems. We also apply the results of our research to areas of national priorities for various industries, other government agencies, academia, and other laboratories in NIST. Some recent accomplishments follow.

Measurement Science - Method Extension and Development. In the environmental arena, we continue major programs in atmospheric measurements, standards, and pollutant identification. We increased the precision and accuracy in low level counting for measuring radionuclides (e.g., ^{14}C, ^{3}H, and noble gases) of interest in environmental science using individual pulse analysis (pulse amplitude, shape, time of occurrence). These studies tie the data stream to physico-chemical knowledge of the counting process and show promise that the 0.5% precision and accuracy required in radionuclide measurements can be achieved.

Leading-edge measurements in determining isotopic ratios of carbonaceous gases and volatile organic compounds were used to develop a reliable method for measuring carbon isotopic distributions on samples as small as 7 μg, and with accuracies of 1% for 25 μg and 0.1% for 1500 μg samples using our gc sample preparation method with accelerator mass spectrometry. This work was done collaboratively with Woods Hole Oceanographic Institute. Additionally, working with colleagues in California, we used these same techniques to identify restaurant cooking (in addition to vehicles, paved road dust, and wood burning fireplaces) as a major source of urban contemporary carbon contributing to pollution in the Los Angeles Basin. The New York Times subsequently reported that restaurants in the area emit ~33 tons of particulates and volatile organic compounds per day, suggesting emission controls are needed to help solve the LA basin pollution problems.

We have also developed (with EPA) a new NIST/EPA method for analysis of airborne asbestos and are publishing NIST Internal Reports on various aspects of the method. Those published this year include: evaluation and analysis of air filters, new fiber counting rules, verified asbestos analysis, and standard reporting forms. Future documents will include uncertainty estimates and the reporting of results; use of control charts; methods for etching filters; and fiber identification.

Finally, several Primary Standard Reference Ozone Photometers used for national and international ozone monitoring, were updated and calibrated against the NIST primary instrument. Photometers were built for Canada and the Czech Republic. We continue to get inquiries from foreign governments (NPL in England, Germany, France) about the photometer.

The capability to focus x-rays at the 1-100 μm spatial scale for chemical analysis will facilitate industrial measurements in advanced alloys and electronic devices. To establish this capability, we designed and built an x-ray "optical" test bench to investigate x-ray focusing optical elements, to determine measurement parameters, and to test this technique on industrial materials. The bench has an x-ray source, translation stages for the x-ray focusing elements in the x, y, and z directions, and a detector with 30 μm resolution (to be increased to 8 μm). We are working with industry through CRADAs to test and improve the x-ray focusing optical elements.

To develop optical/neutron techniques as probes for surface chemistry, we investigated the interactions of the prototypical refrigerant 134a (CF_3CFH_2) and its isomer 134 (CF_2HCF_2H) with the zeolite NaX to determine bonding and dynamics. By combining these results with those from non-linear optical (NLO) techniques, we anticipate that algorithms can be developed to aid in the selective synthesis and separation of environmentally benign products. Other NLO studies on semiconductor thin-film oxide/GaAs interfaces suggest applications for contactless *in situ* wafer diagnostics. In a related study on surface reactions with free radicals, we are characterizing the incident energy dependencies of radical-surface reactions, of import in plasma processing.

Several new instruments were ordered; these include a new environmental SEM to investigate samples under various atmospheres and partial pressures (10-1000 Pa); a new field emission AEM for our trace nanoanalysis efforts; an atomic force microscope (AFM/STM combination), which, in conjunction with the newly modified scanning scattering microscope, will be used to begin establishing measurement parameters of surface roughness for the production of potential standards with atomic and molecular resolution; and a femtosecond laser amplification system to upgrade and replace equipment owned by the Physics Laboratory.

Measurement Science - Technique Application and Materials Fabrication. Understanding the mechanisms of thin-film growth will lead to improved manufacturing techniques for various industrial sectors. In our magnetic engineering effort, we continued to investigate the growth, structure and magnetic properties of metallic thin films. We provided details on manufacturing magnetic films to industry which resulted in a 40% increase in the giant magnetoresistance (GMR) effect, of basic importance to new generations of magnetic recording media and read heads. Additionally, using a low temperature manufacturing process, we have obtained the largest GMR value to date.

The reliable growth and doping of commercial grade high-T_c films or ferroelectric oxides can be accomplished by understanding surface-related phenomena ranging from growth kinetics to the reactive interactions of the high-T_c film with underlying substrates. Collaborating with the University of Maryland's Center for Superconductivity Research and the Physics Laboratory, we studied doping of $Nd_{(1-x)}S_xTiO_3$ using photoelectron spectroscopy in the vuv using SURF II to follow changes in the hybridization of Ti 3d and O 2p electron states, which can be correlated to structure. Selection of these materials allowed us to measure for the first time by photoemission, the effective mass m^* of the Ti-3d electrons across the metal-insulator transition.

Particle sampling and analysis, including characterization of environmentally hazardous individual particles and populations of particles, constitute a significant effort within the Division. Our continuing studies with automated scanning electron microscopy (SEM) to characterize particle populations have led us to develop an automation algorithm to establish thresholds of particle images, specifically to decrease the effect of human variability on this measurement. We have also shown that a commercial software for determining thin-film elemental concentrations agrees within 2% of results obtained on bulk samples using the NIST-developed FRAME4 correction software. As another aid for the analysis of materials, we embedded rules in an image processing computer program that identify the phases present in materials from elemental compositional mapping results. Future work will involve use of "fuzzy rules" and principal component analysis to aid in interpreting results, and scatter plots to check phase labels on results.

Using the Desktop Spectrum Analyzer (DTSA) developed in the Division, we demonstrated that the increasing practice of "standardless" analyses in electron probe microanalysis to save analysis time, can introduce errors of up to ±100% rather than the well-established and accepted ±1-3%. We have published a paper that shows the errors are so large that results are often meaningless and are beginning to cast doubt on the whole field of quantitative electron probe microanalysis.

In microprobe techniques, we continued our efforts to increase sensitivity and spatial resolution of analyses. In secondary ion mass spectrometry (SIMS), we investigated measurement parameters of 3-dimensional compositional mapping to provide quantitative measurements of surface, near surface, and depth distributions of species in samples. External implanted standards are adequate for quantification of samples that can be sputtered uniformly; however, for samples that sputter non-uniformly, we have ion-implanted boron, which then serves as an internal depth scale standard. This technique is being applied to the 3-dimensional chemical analysis of semiconductor devices, high T_c superconductors, small particles, and biological tissues. Another interesting study (with USDA) identified ^{44}Ca localization in apple tissue structures, which is added to increase fruit shelf life.

Standard Reference Data, Materials, and Protocols are needed to achieve accurate quantitative measurements. We are involved in national and international round robins to test measurement methods and establish procedures for obtaining reliable data. For example, X-ray photoelectron spectroscopy (XPS), one of the most commonly used techniques for determining the chemical states of species present on surfaces, requires careful calibration of binding energy scales. A proposed standard for calibrating these scales was drafted for ASTM Committee E-42 on Surface Analysis, and tested through international interlaboratory comparisons. Related to these efforts is one of the first attempts to develop Standard Test Data (STD) for XPS measurements. STDs are analogous to SRMs in that they establish the accuracy of data algorithms that convert instrument responses to relevant chemical concentration information. Currently, STDs are being developed by modeling measured XPS spectra of the superconductor $YBa_2Cu_3O_7$. Visits to General Motors and Perkin Elmer, as well as a mini-workshop held by staff at the Surface Analysis '94 meeting, have led to the formation of a steering committee to help guide the work towards specific materials and data analysis problems of concern to industrial communities.

Another round robin measurement effort that our staff spearheaded involved 17 laboratories to assess the repeatability and reproducibility of crater depth measurement by stylus profilometry, used extensively to determine sputtering rates and relative sputtering efficiencies in SIMS. These measurements have provided the first estimates of the true uncertainties of the depth scale in a SIMS depth profile.

We investigated production and measurement parameters for a second thin-film quantitative standard, used in analytical electron microscopy. Problems of non-representative ion-beam sputtering and deposition of various elements and sputtering contamination were addressed.

The Particles-in-Oil Standard, being developed in close cooperation with the National Fluid Power Association and its various members, passed a major hurdle in the certification process. The first batch of test materials, developed by a member of the Association, showed unacceptable bottle-to-bottle inhomogeneities. A research program was undertaken and the preparation process modified to produce a second batch of material with homogeneities within the target goal.

Other SRMs, materials, or data that are undergoing development include: the reissue of SRM 2135, a depth-profiling standard consisting of alternating thin layers of Ni and Cr; stable isotope standards and intercalibrations for measuring atmospheric species critical in global monitoring (with IAEA); and the use of on-line databases to access the vast amount of chemical information available for identifying production materials or chemicals.

In addition to the NIST Fellows, our staff received several other honors. David S. Simons received the Department of Commerce's second highest award, the Silver Medal "....for outstanding leadership and innovative accomplishments in quantitative microbeam mass spectrometry". Dale E. Newbury, with Richard Leapman from NIH, received the oldest established NIST award named for Samuel Wesley Stratton "...for developing the unprecedented capability to measure 2-5 atoms at nanometer spatial scales." This is the first time an internal NIST award has been shared with another agency, and underscores our outside collaborations in research to define the state-of-the-art. Additionally, a Measurement Services Group Award was received by Eric B. Steel, Diane J. Hues, John M. Phelps, Shirley Turner, Jennifer Verkouteren, and Eric S. Windsor for their extraordinary efforts during the past several years to develop accurate asbestos measurement techniques, produce five new and two recertifications of existing asbestos SRMs, and provide the technical basis for the Congressionally mandated accreditation program under Asbestos Hazard Emergency Response Act (AHERA).

Staff in the Division received two patents. Strong interactions by the staff with our constituents and effective technology transfer are shown by substantial technical outputs (see Section VI. C), participation on 15 editorial review boards, close interactions with national (e.g., ASTM, ANSI, MAS, EMSA, NFPA) and international (e.g., ISO, IUPAC, IAEA, VAMAS) organizations, and participation on established committees. In addition, staff participated on evaluation and consulting panels for DoE, DoD, NSF, EPA, NRC, USGS, WHOI, and industrial groups. Finally, we have organized, co-organized, or participated in several international and national conferences. Information on selected technical contributions can be found in the following section.

B. Selected Technical Reports (Surface and Microanalysis Science Division)

1. Improved Calibration of the Binding-Energy Scales of X-Ray Photoelectron Spectrometers

C.J. Powell

X-ray photoelectron spectroscopy (XPS) is one of the most commonly used techniques for surface analysis. The principal use of XPS is to identify the elements present and their chemical state in the outermost several atomic layers of a solid specimen. The reliable determination of chemical state depends on measurements of small changes in the positions of photoelectron and Auger-electron peaks; these changes typically need to be determined with an accuracy of better than 0.1 eV. Recent interlaboratory comparisons, however, have shown that many instruments in practical use were not calibrated with sufficient accuracy to enable the "chemical" shifts to be determined with the needed confidence.

We drafted a proposed standard for the calibration of the instrumental binding-energy (BE) scales of XPS instruments for consideration by ASTM Committee E-42 on Surface Analysis. The draft assumes initially that the BE scale is linear and can be calibrated at two points (one at a low BE and the other at a high BE) using reference BE values. The calibration and the assumption of BE-scale linearity are then checked using measurements of designated photoelectron and Auger-electron peaks at intermediate points on the BE scale.

An interlaboratory comparison was conducted recently to evaluate the convenience and reliability of the draft standard. This intercomparison involved measurements on eleven different instruments and a wide range of operating conditions. While the draft standard was found to be generally satisfactory, two useful results were obtained that will lead to improvements in the standard. First, different operators used the available instrumental software in different ways to locate peak positions leading to variations of up to about 0.05 eV in the derived peak positions. Second, it was found that the positions of Auger-electron lines on the BE scale were slightly different (about 0.13 eV) depending on whether the measurements were made on instruments with or without an x-ray monochromator. This systematic difference is due to the different average energies of characteristic aluminum Kα x rays from the two types of x-ray sources. Revisions will be made to the draft standard for both these observations.

The draft standard has also been used in the evaluation of elemental BE data from four major sources. The BE scales for three instruments had not been adequately calibrated, but they were calibrated retroactively using the standard. Comparison of the corrected BE values showed a generally high degree of consistency for most elements (although there were several outliers that could be attributed to differences in specimens or to possible mistakes). The mean elemental BE values from this comparison will be used for the estimation of chemical shifts in Version 2 of the NIST x-ray photoelectron spectroscopy database.

The zero point on the BE scale has previously been identified as the inflection point in the Fermi-edge region of a valence-band photoemission spectrum of nickel [which has a conveniently high density of states (DOS) in the vicinity of the Fermi "edge"]. This method is expected to be reliable when the DOS distribution is close to rectangular; but this is not the case for nickel. Experiments and simulations have been conducted that show differences of up to 0.05 eV, depending on the energy resolution, between the inflection points for nickel and silver (which has a rectangular DOS). Revisions will be made to the reference BE values to remove this systematic error.

2. Characterization of Errors in "Standardless" Electron Probe X-ray Microanalysis with NIST Desktop Spectrum Analyzer (DTSA): Short Cuts Can Be Dangerous to Your Results

D.E. Newbury

Rigorous quantitative electron probe x-ray microanalysis is based upon determining the intensity ratio between a characteristic x-ray peak in the unknown to the same peak in a standard measured under identical operating conditions of beam energy, known dose, detector efficiency, and specimen orientation and position. This ratio of intensities, known as the "k-value", forms the starting point for quantitation. To a first approximation, the k-value is proportional to the ratio of concentrations between the unknown and the standard. The ratio of measured intensities differs from the ratio of concentrations because of matrix (interelement) effects: electron backscattering, electron stopping power, x-ray absorption, and secondary fluorescence, which all depend on sample composition. Theoretical and empirical methods exist to calculate the complex electron/x-ray physics that form the basis of these matrix corrections. These methods permit analysis of unknown multi-element compositions based upon the use of standards that can be as simple as pure elements. The more than 40 year history of the development of these quantitative microanalysis procedures has included extensive testing through the measurement of homogeneous multi-element samples whose composition was characterized by independent analytical techniques. The distribution of relative errors from these studies is characterized by a standard deviation of 1-3%, depending on the matrix correction method used.

In recent years, the "standardless" method of quantitative analysis for energy dispersive x-ray spectrometry has been widely promulgated as a more efficient approach. Standardless analysis requires only the measurement of the x-ray spectrum of the unknown. The intensities of the required standards for k-value determination are calculated directly from a first principles theoretical description of x-ray generation, propagation, and detection, or indirectly from experimental fits to a database of measured standard intensities. To date, no studies have been published of the distribution of errors that results from any of the standardless analysis procedures. By analyzing a wide range of NIST SRMs, glasses, and stoichiometric binary compounds, we have determined such an error distribution for the first principles standardless analysis procedure incorporated into NIST Desktop Spectrum Analyzer (DTSA). Compared to the conventional approach to quantitative analysis, the error distribution observed for standardless analysis is extremely wide, with errors ranging over ±100% relative, more than an order of magnitude greater. The relative errors are so large, in fact, that standardless analysis results are often not useful in determining the formula of a compound based on the measurement of all major constituents. This result is not surprising in view of the uncertainties that exist in the ionization cross section and fluorescence yield, particularly when different atomic shells are considered, and in the detector efficiency. However, the real consequence of blindly trusting standardless analysis is that confidence in the technique of quantitative electron probe x-ray microanalysis is actually decreasing because of the unacceptably large errors that result from the standardless short cut.

3. Standard Test Data for Quality Assurance in Surface Science Spectra

J.M. Conny, L.A. Currie, and C.J. Powell

Standard test data (STD) are simulations of analytical instrument responses that help determine the veracity of data analysis algorithms for converting instrument responses to relevant chemical information. In the paradigm of the analytical measurement process, STD are used to calibrate, or control the quality of, the data evaluation domain, while Standard Reference Materials (SRMs) are used for calibration or quality control of both the sample preparation/measurement domain and the data evaluation domain. Unless the composition and structure of the SRM and the sample are sufficiently similar, however, confounding interference and matrix effects or systematic errors that appear only during sample measurement may lead to inaccuracy or imprecision without the knowledge of the analyst. Within the data evaluation domain, STD may be used to detect and control such inaccuracy and imprecision because errors and matrix effects are included in the simulation of sample measurement.

We have focused on developing STD for the surface analytical technique, X-ray photoelectron spectroscopy (XPS). The purpose is to provide well-defined spectral data for testing software procedures that detect, locate, resolve, and measure the intensity of peaks from XPS instrumentation. As standard test data, modeled XPS spectra may help the surface analyst determine which data analysis algorithms to use in specific circumstances, such as the type of smoothing, background correction, curve-fitting and curve synthesis procedures, or determine the order that algorithms should be run (e.g., data filtering, curve-fitting). Also, modeled XPS spectra may help the analyst assess data handling and analysis software performance, such as determining the reliability of peak detection *and uncertainty estimation* for parameters calculated in curve-fitting.

Currently, we are modeling measured XPS spectra of a $YBa_2Cu_3O_7$ superconducting thin film that have been well studied and reported in the literature. To address the resolution of overlapping peaks in the oxygen 1*s* spectrum, STD modeling involves several steps: 1) removal of noise and systematic error by methods such as Savitzky-Golay smoothing and Fourier filtering; 2) fitting functions to the data such as splines and Gaussian/Lorentzians; 3) modifying the intensities and shapes of overlapping component peaks in the model by modifying the functions; and 4) simulating noise and systematic error with the same character (e.g., white, 1/f, low-frequency) as the measured spectra. By generating multiple STD spectra containing the same chemical information defined by the fitted functions but different random error, sets of STD spectra may be analyzed to determine statistically the veracity of data analysis algorithms.

Following visits to Physical Electronics, Inc. and General Motors Corp., plus a mini-Workshop on the topic, we have formed a steering committee to help guide the work toward specific materials and data analysis problems that are of particular concern to the instrument manufacturing and corporate research communities.

4. Impact of the Chemical and Isotopic Blank on Interpretation of Environmental Radiocarbon Results

L.A. Currie, D.B. Klinedinst, B.A. Benner (835), and G.A. Klouda

The chemical blank sets the fundamental limit to low level concentration measurements, and quantitative treatment of the distribution of the blank is essential for the reliable estimation of uncertainties of chemical results. In most cases blank estimation and correction is a simple linear (subtractive), univariate process, so that confidence intervals can be computed according to the conventional rules of "error" propagation. However, in the investigation of isotopic and organic chemical patterns of carbonaceous aerosols in Roanoke, VA (in the NIST-EPA project to apportion sources of atmospheric mutagens among motor vehicles, woodburning, and fuel oil combustion), we found conventional treatment of the blank to be totally inadequate.

The experiments involved the use of ^{14}C as a unique fossil/biomass source discriminator, and complementary patterns among dimethyl phenanthrene (DMP) isomers for further discrimination among sources. Since the results of these experiments depended on isotopic/chemical patterns, or ratios, the treatment of the blank and its variability necessarily became a multivariate problem. This introduced the added complication of covariance among blank components, an issue that does not arise in single analyte blank correction. To further complicate the matter the bivariate or multivariate blank correction function is non-linear, with the consequence that the simple Taylor expansion route to uncertainty estimation is inadequate, and further, that the final error distribution is non-normal and asymmetric. Our approach was first, to obtain an adequate number of actual blanks to estimate the blank covariance matrix, and second, to employ a Monte Carlo approach to propagate this covariability -- e.g., of ^{14}C and ^{12}C -- through the non-linear blank correction function. The impact of these factors was severely dependent on the number of degrees of freedom, such that fewer than approximately five independent bi- or multi-variate blanks resulted in very serious uncertainty inflation.

The results showed that, for the lowest concentration samples, the blank covariability totally dominated the uncertainty derived from the accelerator mass spectrometer isotopic measurements and the gas chromatograph mass spectrometer isomeric measurements. For example, the uncorrected fraction of modern carbon derived from the $^{14}C/^{12}C$ ratio for Roanoke aerosol sample #50121 had a symmetric expanded (90% confidence level) uncertainty interval of 0.76 ± 0.03; Monte Carlo uncertainty estimation for the blank corrected isotope ratio gave an asymmetric (90% confidence level) interval of 0.88 (-0.14, +0.07). Reliable uncertainty estimation for the multivariate, non-linear, blank dominated case is extremely important, because of intended uses by the data recipients, such as source apportionment, regulatory decision making, and elemental tracer model validation.

An extra dividend of the availability of both isotopic and isomeric patterns for the series of Roanoke blanks was the possibility of *apportioning the blank.* In fact, combined multivariate analysis of the suite of DMP isomers and carbon isotopes showed that the sequence of blanks followed a 2-component mixing curve having petroleum and hardwood combustion aerosol end members.

5. Fast Pulse Shape Acquisition System and Individual Pulse Analysis for Low-level Decay Counting

G.A. Klouda, E.M. Eijgenhuijsen (Twente Technical University, The Netherlands) and L.A. Currie

The need for high accuracy, low-level counting (*llc*) of radionuclides, e.g., ^{14}C, ^{3}H, and noble gases, is becoming greater especially in the field of environmental sciences. To reach the precision levels often required of such measurements (0.5%), it is critical to link the characteristics of the data stream (pulse amplitude, shape, and time of occurrence) to physicochemical knowledge of the counting process. For example, the stability of proportional and Geiger-Müller counters have been studied for transient and after-pulse events under normal background conditions or given the presence of an impurity, e.g., O_2, at 10^{-5} to 10^{-4} levels. We have demonstrated that utilization of time series and distributional analysis of the individual pulses can expose control problems that could not possibly be detected by conventional low-level quality control techniques, such as those based on control charts of segmented counts, or computation of the Index of Dispersion. An example of the impact of individual pulse analysis (IPA) arose in the investigation of transients in long term measurements. A total of 689 counts were collected in 64.85 hours, for an average rate of 10.62 counts per hour with a Poisson relative standard deviation of 3.8%. Subdividing the time into 10 equal segments indicated an early, high rate transient, but it could not, of course, pinpoint the time of onset or disappearance of the transient. IPA, however, showed immediately that the transient was present at the start, and was essentially gone after 3 hours. Variations among the remaining 9 segments showed no significant deviations from Poisson counting statistics. Again, IPA applied to the entire data stream, gave new insight: it showed that there was an unsuspected dead period of 2.63 hours after about the 14th hour of counting. Undetected, the dead period would bias the results low by 4.1%, whereas the detected, but not pinpointed, positive transient biased the results high by 12.0%.

Full utilization of individual pulse shape and time series analysis (IPA), however, has thus far been restricted to low count rate experiments because of data transfer rates. A major research and development focus has therefore been to develop an all new (faster) IPA system to meet the demands of much higher count rate experiments (100s cpm) than previously studied. The existing 486 33MHz PC has been extended by adding 72 Mb of memory and an on-board internal 100 MHz oscilloscope card. This system is capable of digitizing, time stamping and storing incoming pulses in a short enough time (300 μs) to ensure that no pulses are lost at the current count rate of interest. Software has been developed in ANSI C for full automatic set-up of the waveform analyzer and run-time (on the fly) evaluation of counter performance including energy, rise time, and time of occurrence (pulse distribution), as well as plateaus and other calibration procedures.

Also, the original system is still set up to acquire event data for comparison with data obtained from the new system. This compatibility between old and new systems will be valuable during our next phase of development, *i.e.*, the evaluation of the new system in terms of reliability and the establishment of benchmarks for performance.

6. Improved Isotopic Measurements for Carbon-13 Analysis

R.M. Verkouteren

Gas isotope ratio mass spectrometry is an important method for investigating the natures and sources of materials, and recent advances in instrumentation and automation have improved intralaboratory measurement repeatability (1-sigma) to less than 0.001% (0.01‰) for differential measurements of stable carbon isotope ratios. Differential isotope ratios between samples (*sam*) and standards (*std*) are expressed using the *delta* (δ) notation, where $\delta^{13}C$ (in ‰) = $1000 \cdot [\{(^{13}C/^{12}C)_{sam} / (^{13}C/^{12}C)_{std}\} - 1]$.

The calculation of $\delta^{13}C$ is normally accomplished through the measurement of three isotopic forms of CO_2: the mass 44 isotopomer ($^{12}C^{16}O^{16}O$), mass 45 isotopomers ($^{13}C^{16}O^{16}O + {}^{12}C^{16}O^{17}O$) and mass 46 isotopomers ($^{12}C^{16}O^{18}O + {}^{12}C^{17}O^{17}O + {}^{13}C^{16}O^{17}O$). This method requires the assumption that ^{17}O and ^{18}O abundances in CO_2, for *all* samples and standards, are exactly related through an oxygen isotope fractionation constant (α). However, recent measurements of the α "constant" indicate an α distribution rather than a discrete value; this distribution places variance and uncertainty onto the calculated $\delta^{13}C$ values. We have demonstrated, using Monte Carlo methods, that the natural variation in α leads to a standard uncertainty of 0.053‰ in $\delta^{13}C$, similar to the reproducibility observed in prior interlaboratory comparisons of isotopic CO_2 reference materials.

We have developed a new approach to $\delta^{13}C$ determination that is independent of the natural variation in α. Our isotope ratio mass spectrometer is uniquely capable of measuring a fourth isotopic form of CO_2, mass 47 isotopomers ($^{13}C^{16}O^{18}O + {}^{13}C^{17}O^{17}O + {}^{12}C^{17}O^{18}O$), along with isotopomers of masses 44-46. This measurement information then allows us to calculate $\delta^{13}C$, without assumptions, through a reduction algorithm of our design. This approach is limited by the instability of the scarce mass 47 ion beam (normal CO_2 contains 0.0048% of mass 47 isotopomers) and sensitivity to isobaric contamination. We have modified our mass spectrometer to optimize the reproducibility in differential CO_2 measurements by up to a factor of four, resulting in $\delta^{13}C$ values with standard uncertainties of 0.043‰, an improvement over the 0.053‰ uncertainty from the usual method of $\delta^{13}C$ measurement. An important application of this method is the $\delta^{13}C$ measurement of isotopic CO_2 reference materials to determine the true values of α for these materials, information required to decrease uncertainty intervals of normal measurements. A special application is the $\delta^{13}C$ measurement of stratospheric carbon dioxide, an important atmospheric tracer gas that can exhibit significant non-mass-dependent isotopic fractionations of the oxygen isotopes that preclude normal measurement methods.

7. Comparative Study of Fe-C Bead and Graphite Target Performance with the National Ocean Science's Accelerator Mass Spectrometer

D.B. Klinedinst, A.P. McNichol (WHOI), L.A. Currie, R.J. Schneider (WHOI), G.A. Klouda, K.F. von Reden (WHOI), R.M. Jones, and G.A. Jones (WHOI)

The urgent need in the environmental sciences to determine ^{14}C in ever smaller samples led to a collaborative study between the Woods Hole Oceanographic Institution (WHOI) and NIST. The two organizations face important scientific questions involving carbonaceous matter in the oceans and the atmosphere that demand a "microgram radiocarbon dating" capability. In pursuit of this, an accelerator mass spectrometry (AMS) experiment was undertaken that matched the state-of-the-art high precision, high intensity AMS capability at WHOI with our ability to prepare rugged, microgram-level carbon targets with low chemical processing blanks. The experiment was designed to evaluate precision, accuracy, and stability as a function of carbon mass, taking into account the effects of such factors as the sample fraction of modern carbon (f_M), target type (graphite *vs* iron-carbon bead), and blanks. The findings were positive, showing that precision, accuracy, and stability were adequate to determine ^{14}C to 1% or better in samples containing as little as 25 µg carbon. Results indicated no significant difference in average performance of the two target types at the intercomparison level (500 µg carbon), though individual targets showed reversals in stability and precision. The Fe-C bead targets proved sufficiently rugged in the AMS recombinator ion source to achieve stable and precise performance with as little as 7 µg carbon, and an uncertainty ranging from 1% modern carbon or better at 25 µg to 0.2% modern at 1500 µg carbon. A small but significant mass dependence of the modern carbon calibration factor was observed, requiring mass matching standards for the achievement of extended accuracy for the smaller samples. Finally, we observed significant processing blank variability (0.03 - 5.0 µg carbon) which is the ultimate limiting factor for the smallest samples.

8. NIST X-Ray Optical Test Bench for Microfocussing

T. Jach and S. Thurgate (Murdoch University, Australia)

In recent years we have witnessed the rapid development of optics that operate at x-ray wavelengths. This is largely due to progress in the fabrication of smooth curved surfaces and in the deposition of uniform thin films of precise thicknesses. An important application of optical elements is the collection and focussing of x-rays from conventional sources into concentrated spots which permit the analysis of very small areas by element fluorescence and x-ray diffraction.

The choice of available optical elements for this purpose is diverse. They include single capillaries which taper to microscopic dimensions, layered synthetic multilayers (LSMs) fabricated on multiple spherical surfaces, capillary bundles which are organized to aim the collected x-rays onto a single focal spot (Kumakhov lenses), and layered synthetic multilayers on compound surfaces. Our goal has been to use these devices to focus x-ray beams down to microscopic spots of concentrated intensity for the purpose of microanalysis. To this end we have completed an x-ray optical test bench that can evaluate the characteristics of optical elements in several important ways.

The test bench uses a conventional copper x-ray source with radiation principally at 8 keV. The optical element is mounted on a precision stage, computer-controlled by stepping motors, which allows translation in x, y, and z-directions as well as rotation in two axes. The optical element is positioned in the x-ray beam and the degree of x-ray collection and focussing is observed downstream by an imaging detector. Our current detector uses a fluorescent screen with an image intensifier to convert the x-rays to visible light. The light is magnified and imaged onto a CCD camera, from which the image is stored on a computer for further analysis.

It is desirable to characterize an x-ray optical element not only for the size of the spot attained, but also for its spot intensity, aberrations, and scattered radiation. Our present detector allows us to observe x-rays at very low intensities, fewer than 40 photons/second in an area of 300 μm diameter. Since our goal is to produce the maximum intensity of spot possible, a large dynamic detection range is desired. Thus, we have gone to fluorescence optical conversion. The resolution of the detector is 30 μm, and the precision of our optical stages is 10 μm. A second integrating imaging detector will be added during the current year which will permit us to go to 8 μm resolution. Our aim is to evaluate focal spots in the 100 μm to 10 μm diameter range.

During the coming year we plan to evaluate optical elements of the types listed above. We are collaborating with industrial, government, and university sources, including X-Ray Optical Systems, an ATP recipient. Aside from obtaining the best means of concentrating radiation for our own and industrial microanalysis, we wish to provide guidance to the industrial developers of x-ray optical elements which will allow them to improve the performance of these devices.

9. Procedures for Thin-Film Analysis with the Electron Microprobe

R.B. Marinenko

Thin films of predictable composition, thickness, and homogeneity are being produced for applications in superconductors, electronics, process sensors, etc. Routine characterization of such films on the micrometer scale can be done with the electron probe microanalyzer (EPMA). A commercial data reduction program, STRATA, is available which uses a routine that calculates the film thickness as well as the composition of the film from element k-values (ratio of the background-corrected x-ray intensity of the unknown to that of a standard) obtained at several voltages. We have been using this program for the analysis of thin films such as high T_c superconductors and Ba(Sr)TiO_3. We validated our thin-film measurements using a well-characterized film that was thick enough to be treated as a bulk specimen at low voltages.

A Ba-Ca-Cu-O thin film, 0.46 μm thick, was measured with EPMA using wavelength dispersive spectrometry (WDS) at excitation potentials of 12.5, 15, 20, and 25 kV. At these voltages, elements from both the film and the substrate ($LaAlO_3$), were detected. The element concentrations were calculated with STRATA from k-values determined at these voltages. SRATA uses an XPP $\phi(\rho z)$ correction procedure. At 10 kV only the elements of the film were detected; elements from the substrate were not observed. K-values determined at this lower voltage were used in FRAME4, a ZAF (atomic number, absorption, and fluorescence) data reduction routine developed in this laboratory for bulk specimens. In addition, at all five voltages the heterogeneity of the film was determined to be less than 1.1 percent from ten independent samplings taken using a 5 μm beam and a 100 nA current.

Results from the two different data reduction procedures, FRAME4 and STRATA agreed with less than a ±2 percent relative error for the three cations. STRATA, therefore, yields similar accuracy and reliability as a bulk specimen program such as FRAME4. The results from both routines also agreed with independent RBS (Rutherford backscattering) and PIXE (Proton Induced X-ray Emission) results with less than the ±3 percent relative error assigned to these latter techniques. The agreement within these error limits demonstrates that the STRATA data reduction routine can be confidently used for thin film analysis. In the future additional well-characterized films will be analyzed.

10. The Analysis of Airborne Asbestos by Transmission Electron Microscopy

S. Turner, E.S. Windsor, and E.B. Steel

In 1986, Congress passed the Asbestos Hazard Emergency Response Act (AHERA) mandating that the nation's schools be checked for the presence of asbestos. In response to that legislation, the U.S. Environmental Protection Agency (EPA) in 1987 wrote the AHERA method for determining the presence of airborne asbestos. This method has been tested over the past seven years by more than one-hundred laboratories performing analyses for clients and by round robins and proficiency testing conducted in association with the NIST accreditation program. Through this testing, it became evident that the AHERA method could be improved and clarified. We have been working with the EPA to develop and test a new method for the analysis of asbestos in air. This method will take the form of several procedures that are documented in NISTIRs (Interagency Reports). In the last year, work was completed on several of the procedures; a summary of their content and the reasons for the publication are listed below:

NISTIR 5134: A procedure for evaluation and analysis of air filter preparations is given along with a description of sample preparation artifacts. Round robin studies and proficiency tests had shown that laboratories have sufficient difficulty with the sample preparation procedure to bias their results significantly.

NISTIR 5350: A new method for counting asbestos collected onto filters is described. The laboratories had difficulty interpreting the counting rules given in the AHERA method in a consistent fashion. Round robin studies showed that the simplified version given in this IR vastly improves the precision of the analyses.

NISTIR 5351: A method for performing verified analysis of asbestos is described. This procedure is important for training and evaluating the performance of analysts in their counting of asbestos.

NISTIR 5358: A standardized form for recording results of analyses is given. This will aid interlaboratory comparisons and the conduct of proficiency tests and verified analyses.

A substantial amount of work has been devoted to development of other procedures for the NIST method. A method for reporting uncertainty of results is being developed that is based on a bootstrapping procedure. For the bootstrapping procedure, it is not necessary to assume a distribution for counts which was problematic in previous procedures. Because of numerous inquiries from laboratories, NIST is developing a guidance document for use of control charts. Additional work is planned for the next year on methods for etching filters, identification of fibers, and for reporting results.

11. Variable Threshold Settings for Automated Electron Microscopy

J.A. Small

The analysis of large numbers of particles by automated scanning electron microscopy (ASEM) is often used in conjunction with multivariate-analysis algorithms to classify particles into different groups based on size, shape, and elemental composition. These groups and the number of particles belonging to each can then be used for the macroscopic characterization of a sample. For example, automated electron probe analysis is often used to model atmospheric systems where ASEM is used to identify the various sources based on particle shape and composition, natural and anthropogenic, that contribute to an atmospheric particulate sample.

One of the most important parameters that must be adjusted by the analyst during an ASEM run is the threshold setting for the particle images used during the analysis. The threshold setting determines not only which particles are selected for analysis but also dramatically influences the determination of particle size and shape. In addition, current algorithms allow only a single threshold setting which is then used for all the images collected during an analysis. Thus, any shift in image intensity may result in errors in particle number and size.

During this past year, we have conducted studies of image thresholds using both experienced and inexperienced analysts. The results from these studies show that there is a wide variation in threshold settings from analyst to analyst and dramatically different values for particle number and size from the same image.

We are developing an automation algorithm for setting image thresholds. This procedure uses a mathematical fit to the image-intensity histogram combined with a minimum particle area to determine the threshold setting for each image used in an analysis. When implemented, this algorithm will provide a robust threshold that will be operator independent and will be set separately for each image analyzed.

12. Chemical Phase Identification in Materials from X-ray Maps Using Image Processing Software

D.S. Bright

Our Compositional Mapping Program involves making micrographs of samples, where the intensity information denotes the concentration of a particular elemental constituent. As in a conventional electron micrographs, the morphology of the sample is usually still evident. These micrographs typically are electron probe x-ray maps, and are generally multi-variate in that the data consist of registered images showing several individual elements. The objective is to combine these individual element maps and provide images of the chemical species present, of great importance to scientists in many technologies, e.g., for determining the chemical structure of superconductors and advanced alloys.

A sample near chemical equilibrium may consist of crystalline grains of various chemical phases with uniform composition within each grain or region. Grain structure will be seen in the gray level display of the images, but it is difficult to make visual sense from several images of this type. Color composites, that is red-green-blue overlays of any three images, more clearly show the spatial distribution of the phases, where a different shade or color corresponds to each phase. However, the color overlay works for only two or three images at a time. Further, the particular phases are not identified as such, but only discerned by the eye as regions of differing color.

An informative way to visualize the combined images is to assign a label for a particular phase to each pixel of the image. The stoichiometry for each phase in the sample gives a value for corresponding pixels in each image that must be matched for each phase. Due to experimental uncertainties, the concentrations must be given ranges, rather than specific values. Software has been developed to apply rules to make color labeled images showing the chemical phases of samples. The number of rules is equal to the product of the number of phases times the number of elements; e.g., a set of six images (of six elements) of a ceramic sample with nine possible phases has up to 56 rules. The software facilitates this task by allowing the rules to be expressed as equations, as table entries, or as adjustable sliders, which show the selected regions of the appropriate elemental image, and then the result of the change in the over-all phase labeling. Pixels falling on voids in the sample or on boundaries between phases will not fit the rules for any phase (unless they are very broad), and are labeled "not identified". If the rules are too broad, a pixel may qualify for more than one phase, and is labeled as "label conflict".

The rules for some phases more naturally use ratios of elemental concentrations than just concentrations of one single element. The image processing software allows for this by forming secondary images that are arithmetic functions of the original images, and then using the secondary images within the rules.

Future work will involve software development to allow the use of fuzzy rules and to incorporate checking of results with phase-labeled scatter plots. We will incorporate principal component analysis for generating secondary images when the stoichiometry of the sample is not known.

13. Metal-insulator Transitions in Advanced Oxide Materials

S. Robey, V. Heinrich (Yale University), and B. Eichorn (University of Maryland)

Oxides, in particular, transition metal oxides exhibit a wide variety of magnetic and transport properties that find use in a broad range of applications. For instance, $SrTiO_3$ is useful as a high dielectric constant insulator. $BaTiO_3$ is a ferroelectric material that is being investigated for non-volatile memory applications and, along with $LiNbO_3$, may be applied in optoelectronics as a doubling material and for modulators and filters. Understanding the microscopic origins of these properties, thus providing information on possible optimization strategies in materials synthesis, requires information on the electronic structure of these oxides. Many of these materials are not adequately described within the self-consistent-field one-electron picture that has proved so successful in simpler systems. It is thus important to determine the role of many-body effects. Photoelectron spectroscopy provides a direct means of accessing this information.

One of the most important methods of varying properties in these system involves "doping", or substitution of one cation for another. This year we expanded our studies of ferroelectric oxides (e.g., $BaTiO_3$, $SrTiO_3$, etc.) and high T_c cuprates to investigate effects of doping in correlated oxides. This work is performed in close collaboration with the University of Maryland Center for Superconductivity Research where materials synthesis and transport and magnetic characterization are performed. Photoelectron spectroscopy measurements in the vacuum ultraviolet are then performed using the NIST SURF II synchrotron. $Nd_{1-x}Sr_xTiO_3$ was chosen as a prototype highly correlated system which exhibits a composition controlled metal-insulator transition. Substitution of Sr for Nd leads to a transition from a highly correlated Mott-Hubbard insulator ($NdTiO_3$) to a correlated metallic phase for values of $x \sim 0.25$ to $x \sim 0.95$. Using resonant photoemission techniques, we were able to follow changes in the hybridization of Ti 3d and O 2p electronic states. These could be correlated with crystal structure information from x-ray diffraction work at Maryland to provide a picture of the effect of structural changes on the electronic structure.

In addition, careful decomposition of the Ti 3d spectral function allowed us to extract values for the effective mass, m^*, of the Ti 3d electrons across the metal-insulator transition and follow its development until it diverges at the transition point. The effective mass is a fundamental quantity that reflects the degree of importance of many-body effects. To our knowledge, this is the first measurement of m^* using photoemission. Although this measurement represents a special case - the system studied in this work was chosen to optimize the possibility of measuring m^* in this manner - comparison of values obtained by photoemission and those from transport determined at the University of Maryland should provide insight into the validity of the assumptions that must be made in these techniques to determine m^*.

14. Manufacturing Processes for Magnetic Thin-Films

W.F. Egelhoff, Jr., Y. Kadmon (Nuclear Research Center, Beersheva, Israel), D. Misra (University of Pennsylvania), M. Ha, and C.J. Powell

As part of the Magnetic Engineering Competence program, we have provided assistance in manufacturing process engineering to several U.S. companies in the magnetic data-storage industry. In recent years new classes of magnetic thin films have been discovered that have great potential as commercial products. Presently under development by industry are new generations of magnetic recording heads that can read ultra-high-density (1.6 $\mathrm{Gbits/cm^2}$) data stored on hard discs and nonvolatile memory chips. Both products are based on the "giant magnetoresistance (GMR) effect" which is found in certain types of magnetic thin films. Our goal is to help industry learn how to manufacture improved products based on the GMR effect.

In the past year we completed construction of the new "magnetic engineering research facility" which constitutes the most elaborately instrumented thin-film deposition facility in the world. This facility is designed to simulate the magnetic thin-film manufacturing environment and at the same time permit *in situ* application of the most advanced structural and magnetic diagnostic techniques. The facility includes nine magnetron sputter-deposition guns, a complete molecular beam epitaxy system with k-cells and e-beam evaporators, a variety of thickness monitors, a scanning tunneling microscope (STM), ion scattering spectroscopy, reflection high-energy electron diffraction, spot-profile-analyzing low energy electron diffraction, Auger electron and x-ray photoelectron spectroscopies (XPS), and electromagnetic and superconducting magnets equipped for measuring magnetoresistance and magneto-optical properties such as Kerr rotation and ellipticity. A sample interlock and transport mechanism permits in-vacuum access to all parts of the facility.

During the past year we have been studying the details of the manufacturing process for GMR materials in collaboration with ATP-supported U.S. companies such an Nonvolatile Electronics, Inc. (NVE) and the National Storage Industry Consortium (HP, IBM, Digital, Read-Rite, Quantum, and Applied Magnetics). We have found the properties of these materials to be extremely sensitive to almost every detail of the manufacturing process. As a result, most modifications to the current manufacturing processes degrade the performance of the materials. Nevertheless, we have made two important advances this year. We found that we could improve the performance of NVE-type materials by using an aluminum oxide film as a base layer. The second important advance was made when we experimented with a low temperature manufacturing process. We obtained our largest GMR values to date. We are attempting to establish clearly the general applicability of the low temperature manufacturing process to yield improved magnetic performance.

15. Neutron Scattering Probes of Alternate Refrigerants in Zeolites

R.R. Cavanagh, J.M. Nicol (MSEL), T.J. Udovic (MSEL), and M. Crawford (DuPont)

The need for alternative and replacement refrigerants has arisen due to increasing concerns for the damage that chlorofluorocarbons (CFCs) cause to the environment. While significant advances have been made in identifying new refrigerants, economically viable synthesis routes remain a critical issue in the pathway to commercialization of many of the most promising new refrigerants. Key to the development of advanced production methods is the role of surface chemistry in both the synthesis and separation steps. We have initiated neutron scattering studies of the prototypical alternative refrigerant 134a (CF_3CFH_2) and its isomer 134 (CF_2HCF_2H) in the zeolite NaX to establish the binding and dynamics of these molecules in a well-characterized molecular sieve.

All neutron scattering measurements were performed at the NIST reactor in Gaithersburg. Inelastic scattering over the energy transfer range from 30 to 250 meV revealed remarkably different spectral signatures for 134 and 134a when bound in NaX. Initial efforts to develop force fields to account for the data for 134a are encouraging, but analysis of the 134 data has revealed a more complex situation. In the latter molecule, the existence of two conformations is well-known from gas phase measurements, where an energy barrier of 1.2 kcal/mol exists between the anti and gauche configurations. In NaX at 4 K, the neutron scattering data suggest that there are still contributions from two conformers, or possibly a single conformer in multiple binding sites. These data suggest that either the energy difference between the two conformers is reduced in the zeolite, or that the barrier to interconversion is so large as to freeze in the room temperature populations. Raman spectra obtained at DuPont also support this interpretation. During the course of these experiments, a series of measurements of the quasielastic scattering in this system was also undertaken. Results were obtained over the temperature range from 4 to 300 K, with both 4 and 5 Å incident neutrons. While clear dependence on temperature and momentum transfer were apparent, analysis of the entire data set has not established the reorientation dynamics of either 134 or 134a in this system. However, the presence of two types of bound 134 molecules with multiple types of motional dynamics is suggested because of the difficulty in analysis.

Current efforts are focused on combining data from gas phase measurements of the structure and dynamics of the free molecule, with multiple probes of the properties of the molecules inside the NaX pores. From the force field analysis, it is expected that a detailed understanding of the binding and orientational forces within these molecular sieves will emerge. By combining the results of these measurements with current understanding of heterogeneous catalysis, it is anticipated that algorithms can be developed for both the separation and selective synthesis of environmentally benign products.

16. Non-linear Optical Probes of Space Charge Fields in Semiconductors

L.J. Richter, T.A. Germer, and J.C. Stephenson (PL)

Thin-film fabrication is critical to a wide range of technologies, including semiconductor device fabrication, flat-panel displays, opto-electronics, biosensors, and coatings. Emerging applications for these films are placing new demands on traditional characterization tools. Non-linear optical (NLO) techniques have recently been proposed as diagnostics for advanced thin-film applications. NLO techniques share the traditional advantages of linear optical techniques, being contactless, non-damaging, and suitable for *in situ* application. Additionally, due to the nature of the higher-order processes that give rise to the NLO response, NLO techniques are more sensitive than linear techniques to structural details of films and their interfaces. However, unlike the linear dielectric function, which is known to high accuracy for many materials, quantitative studies of the sources of nonlinear polarization are lacking. We have performed NLO experiments on thin oxides of GaAs to assess the sensitivity of these techniques to the electrical properties of thin films.

A critical thin-film issue in semiconductor device fabrication is the deposition of robust passivation layers. An ideal passivation layer serves two functions: it protects the substrate from chemical attack, and it has no trapped charges or interface carrier recombination centers. Oxidation of GaAs has not proven to be a successful passivation method, due to poor electrical properties of the interface. Trapped charge in the oxide layer and at the oxide/GaAs interface produces an electric field in the GaAs that is screened by the interface space charge over a distance that is determined by the GaAs doping level. The electric field lowers the symmetry of the space charge region resulting in finite nonlinear mixing coefficients which are strictly zero in the absence of the electric field. A series of experiments was performed on GaAs substrates of varying doping/space charge region widths to characterize this effect. The perturbations in the NLO mixing were readily detected for the lowest doping levels studied (5×10^{16} cm^{-3}), and for highly doped samples, the perturbations were of order unity. This should be contrasted with the one part in a million change in the linear optical properties that arise from the electro-optic effect.

The sensitivity of the NLO signal to the electric field in the space charge region has been used in experiments of interface carrier dynamics. An ultrafast laser (500 fs pulse duration) is used to inject carriers into the space charge region. The electrons and holes separate in the electric field and screen it, decreasing the NLO response due to the electric field. A second ultrafast laser, time delayed from the first, probes the recovery of the electric field due to the recombination of the carriers. These experiments have successfully demonstrated that NLO techniques can be used to probe both trapped charges (*via* the induced electric field) and interface defects (*via* the carrier recombination velocity) at passivation layers on GaAs. They suggest that NLO techniques could be developed into contactless, *in situ* wafer diagnostics.

17. Hyperthermal H Atom Interactions with Adsorbates on Silicon: The Role of Kinetic Energy

S.A. Buntin

Reactive, unstable atomic and molecular radical species are known to have significant roles in a wide range of heterogeneous chemical processes, including materials processing and catalytic environments. The reaction mechanisms and kinetics of radical/surface processes, however, remain largely uncharacterized. For efficient optimization of present and future process technologies, an understanding and quantification of such reactions is of significant importance.

We have begun a program to characterize the incident energy dependencies of radical reactions on surfaces. Key to this effort is the development of radical sources that are free of interfering impurities and allow for a variable kinetic energy. At the present stage, radicals are generated by excimer laser photolysis in a directed-flow of a suitable radical precursor. Initial studies focused on the kinetic energy dependence of incident H atom abstraction of D atoms adsorbed on a Si(100) surface. This abstraction reaction results in the formation of a surface dangling bond, which is a highly reactive surface site. The initial D/Si(100) surface is prepared on a clean Si(100) surface under ultrahigh vacuum conditions by adsorption of D atoms generated by a hot-filament. With the Si surface maintained at 690 K, the monodeuteride Si(100) 2x1 surface adlayer is formed (i.e., one D atom per surface Si atom with the dimer-pair reconstruction of the clean surface maintained). Nearly monoenergetic H atoms are produced by laser photolysis of hydrogen iodide, and the resultant H atom-induced depletion of adsorbed deuterium atoms on the Si surface is monitored by temperature programmed desorption, which probes the remaining deuterium surface coverage. The incident H atom kinetic energy is varied by selecting different laser wavelengths and polarizations to dissociate the hydrogen iodide. The results indicate that the abstraction probability is identical for 1.0 and 3.3 eV incident H atoms, suggesting that there is no significant kinetic energy dependence for this reaction over this energy range.

With advances in high-speed computing, complete computer modeling of heterogeneous reaction processes is becoming more feasible. In the not-to-distant future, computer modeling, as opposed to present-day empirical methods, may be used to optimize process technologies fully. For this approach to be reliable, however, it is imperative that accurate reaction probabilities and kinetic parameters be available for a wide range of radical/surface reactions. While the present results are relevant to plasma processing of Si, where energetic H atoms may be present in significant abundance, the approach used in these experiments can be extended to quantify reaction probabilities for other radical/surface systems.

18. 3-Dimensional Chemical Microscopy by Secondary Ion Mass Spectrometry

J.G. Gillen

Secondary Ion Mass Spectrometry (SIMS) is a widely used tool for the characterization of elemental species in solid samples. By combining the ion imaging and depth profiling capabilities of SIMS, it is possible to produce 3-dimensional (3D) elemental images of the near surface region of the sample. While qualitative 3D localization of elements has proven to be extremely useful, it is often necessary to determine if an element is present at an appropriate concentration. Therefore, the focus of our work has been on developing the capability for *quantitative* (both concentration and depth scale) 3D elemental imaging.

For materials that sputter uniformly, such as semiconductors, quantification can be achieved by using external ion implant standards. After a 3D image is obtained from the standard, each image "slice" is normalized to a uniformly distributed matrix ion species. The pixels in each image are summed to generate a selected area depth profile. From the known dose of the implant, the integrated counts under the implant peak (after background subtraction), and the depth of analysis, a relative sensitivity factor (RSF) is calculated. This RSF is then applied on a pixel-by-pixel basis to an image depth profile of the same element with an unknown concentration. Unfortunately, many samples we examine do not sputter uniformly. For example, we are interested in trace element distributions in metals. Due to crystallographic effects, we find that each grain of the metal erodes at a different rate. This makes it impossible to assign a unique depth scale to each pixel in the image. Also, each grain gives an analyte secondary ion intensity that is not necessarily related to variations in concentration. To address these issues, we are ion implanting boron at 175.0 keV directly into the sample prior to 3D image analysis. Because the sample has a planar surface, the ion implant will have a peak concentration at a fixed depth below the sample surface (assuming ion channeling effects have been eliminated). The implant peak thus serves as an internal depth scale with its relative position for each pixel in the 3D image serving as the basis for a pixel-by-pixel depth scale calibration. Also, it may be possible to use the boron signal to make a first order correction for the different ion intensities between grains. In addition to the characterization of metals, we are also applying these techniques for the three dimensional characterization of several other materials including semiconductor devices, micrometer-sized particles, and trace elements in biological tissues and in high temperature superconductors.

19. Particulate Contamination on Fuel Valve Seats of Rocket Thrusters

E.S. Etz and R.A. Fletcher

We initiated a project with Intelsat Corporation to solve a crucial analytical problem related to the long-duration flight of satellites in geosynchronous earth orbit. In pre-flight testing of flight-directional rocket thrusters, a particulate contamination residue was found to form on the fuel valve seats of several thruster engines which, in the real space flight scenario, was predicted to cause serious problems, affecting satellites already in orbit over their normal lifetime operations. Intelsat asked for help in identifying this contamination material using the unique molecular microanalysis techniques and facilities at NIST. Their analytical services and at least two commercial contractors were unable to provide answers.

Chemical microanalysis of the contamination residue was performed using infrared (IR) and Raman microspectroscopy, and laser microprobe mass spectrometry (LAMMS). With the IR and Raman techniques, the particulate contaminant was analyzed *in situ,* non-destructively on the steel surfaces of two valve seats. Infrared and Raman results suggested that the contaminant was a complex hydrazone compound product of the reaction of the mono-methyl hydrazine rocket fuel with residues of the CFC cleaning solvent (used routinely prior to the final assembly of thruster engines). For the LAMMS analysis of this material, particles of the contaminant were removed from the valve seat surfaces. The results from LAMMS fully supported the analytical conclusions drawn from the vibrational spectra. These initial results led to laboratory experiments in which the predicted chemical reaction was reproduced under controlled conditions. Products from the experiment were analyzed and the results confirmed the IR/Raman and LAMMS data; the contaminant was formed by the reaction of the rocket fuel with the CFC solvent in the presence of a steel surface.

20. Sputter-deposited Glass Thin Films as Standards for Analytical Electron Microscopy

J.R. Verkouteren, E.S. Windsor, and E.B. Steel

The production of a second thin-film quantitative standard for analytical electron microscopy (AEM) has been investigated. This effort builds on earlier work and is designed to expand the range of elements available in AEM standards, specifically to include elements of higher atomic weight. The films are prepared by ion-beam sputtering of a glass target onto 200+ AEM grids distributed over eight substrate positions on a planetary motion stage. The films must be homogeneous, stable, and have a useful composition. A series of trial runs was conducted to test various experimental parameters for achieving the desired film characteristics.

The composition of the glass target was designed to produce a film with major Al, Si, and Ca, and minor Ti, Mn, and Zn. Past experience had indicated that Zn would be underrepresented in the film, and therefore the target was prepared with the maximum amount of Zn possible. Although 16 wt% Zn was added to the target, the first thin-films produced had Zn concentrations near the detection limit by AEM, which was not considered acceptable in this standard. The ion-beam depositional parameters leading to an increase in Zn in the films were investigated, and the distribution of Zn was mapped across the surface of the stage. The Zn was found to concentrate in the lowermost region of the stage where the total deposits were the thinnest. A retractable shutter that shields the stage during startup of the sputtering process was used to select a portion of the sputtered flux containing higher relative concentrations of Zn.

Additional problems encountered during the trial runs include inhomogeneity and the presence of contaminants. The inhomogeneity may have been due in part to incomplete charge neutralization at the surface of the target, creating unstable beam conditions and discharge to the stage. The problem has been rectified by moving the neutralizing filament as close to the beam as possible. There was significant contamination from the steel chamber surfaces and the Niplated shutter, introducing unacceptable and variable levels of Fe, Ni, and Cr. These problems were solved by covering the affected chamber surfaces and shutter with carbon fabric. The remaining contaminants include argon and molybdenum, from the ion beam and focussing grids respectively, which are unavoidable and do not affect the usefulness of the films.

Although problems were encountered during the trial runs, we believe ion-beam sputter deposition has distinct advantages for producing AEM standards. The films are less than 1000 Å thick, contain the elements of interest within an acceptable range of concentrations, are stable and adhere to the AEM grids, and can be deposited homogeneously over a large enough number of grids to be useful in the preparation of a standard. In addition, the sputtered material can be collected simultaneously on different substrate materials for analysis by independent techniques such as x-ray fluorescence.

21. Particle-in-Oil Standard Reference Material for the US Fluid Power Industry

R.A. Fletcher, D.S. Bright, J.A. Small, E.A. Steel, J.R. Verkouteren, E.S. Windsor, and W.S. Liggett (CAML)

The National Fluid Power Industry has requested NIST to produce a certified Standard Reference Material composed of polydisperse mineral dust suspended in oil for calibrating optical particle counters (OPCs) in terms of particle number size distribution. Optical particle counters are widely used by the fluid power industry to monitor the quality of fluids in hydraulic systems and to test the capacities and characteristics of filters used in hydraulic systems and vehicles (e.g., trucks and cars). The need for a polydisperse mineral standard is derived from governing bodies producing national and international test procedures. Air Cleaner Fine Test Dust (ACFTD), produced in the early 1960's and widely accepted as the *de facto* national and ISO standard for method 4402, is no longer produced nor is it considered adequate under current measurement requirements. The new NIST standard will replace ACFTD and provide a homogeneous material with an accurately determined number size distribution. The NIST standard would become an international standard supported by the National Fluid Power Association. Close collaboration with the Fluid Power Industry is being maintained to aid in the design and ensure the acceptance and use of this proposed SRM.

The particle-in-oil reference material will be prepared from a derivative of the ACFTD Material suspended in MIL-H-5606 hydraulic fluid by a vendor with over 20 years experience in preparing this material. The reference material will be characterized for homogeneity using an OPC (calibrated using a NIST SRM) and accurate number size distribution using a NIST-developed measurement method based on scanning electron microscopy/image processing.

An initial sample of approximately 300 bottles of test material was received, evaluated, and found to be inhomogeneous in particle size distribution across the batch based on the calibrated OPC measurements. We performed collaborative research efforts with the material manufacturer, two filter producers, and an OPC manufacturer to eliminate the inhomogeneity problem. Extensive experimental testing and statistical evaluation were performed and a modified production procedure was developed. A set of 300 bottles produced by this new procedure shows inhomogeneity at the 5% level, which attains the original homogeneity goal. Five batches of material are under production and measurements of homogeneity and number size distribution are planned.

22. Stylus Profilometry Round-Robin for Crater Depth Measurements for SIMS

D.S. Simons

The depth scale of sputter depth profiles obtained by secondary ion mass spectrometry (SIMS) is generally derived by measuring the depth of the final crater with a stylus profilometer, and assuming a constant erosion rate during the profile production. The uncertainty in the depth scale is thus directly related to the uncertainty in the crater depth measurement. This uncertainty has often been quoted to be 5-10% of the crater depth; however, our experience suggests that the error could be considerably less. Therefore, in conjunction with the SIMS subcommittee of the ASTM Surface Analysis Committee E-42, we organized a round-robin interlaboratory comparison to assess the repeatability and overall uncertainty of stylus profilometry measurements. The round-robin also was intended to support a proposed ASTM Standard Guide for Performing Sputter Crater Depth Measurements that is under development. The specimen for the round-robin was a section of a silicon wafer with three separate craters produced by a modern SIMS instrument at NIST, with nominal depths of 0.1 µm, 0.5 µm, and 2.0 µm. Seventeen SIMS labs in North America agreed to participate by making depth measurements on the three craters with their in-house stylus profilometers that had been calibrated with step-height standards. Six separate depth measurements were requested from each of the craters.

The results of the round-robin can be viewed for intra-lab repeatability and inter-lab reproducibility. The median standard deviation for an individual crater measurement was 3.5 nm, with a range from 0.5 nm to 54 nm. The high value was anomalous and indicated that the specific profilometer that produced it needed repair. The lowest standard deviations for a laboratory were not always associated with the same crater. These observations indicate that the random uncertainty is not proportional to crater depth in silicon, but is roughly constant for a specific profilometer. The median relative standard deviation was only 0.18% of the depth for the 2 µm crater, and 3.5% of the depth for the 0.1 µm crater.

The inter-laboratory comparison provides a check of the calibration as well as repeatability. For the 2 μm crater, the relative standard deviation of the mean depth determination among laboratories was 1.2%. This is quite impressive considering that many of the step-height standards had stated systematic error limits of 5%. We compared a commercial step-height standard of 1 μm with a NIST primary standard, and the disagreement was found to be only 0.6%, which was within the stated relative standard deviation of 1% for the commercial standard. The inter-laboratory relative standard deviations for the other craters were 2.5% for the 0.5 μm crater and 4.6% for the 0.1 μm crater. We conclude that the calibration error dominates the overall uncertainty of the depth measurement for the 2 μm crater, whereas the random error component is significant for the 0.1 μm crater. These results have shown that the uncertainty of SIMS crater depth measurements by stylus profilometry is not a simple function of the crater depth, and that it can be on the order of 1%, almost on order of magnitude better than the uncertainties generally accepted for craters deeper than 1 μm.

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Zeissler, C.J., "Particle Analysis: Sample Preparation," Scanning Conference, Scanning, 16, Suppl. IV, IV-17, (1994).

2. Talks

Bennett, J., "The Current Density Profile of a Liquid Metal Ion Source", 7th Annual Workshop on SIMS, Research Triangle Park, NC, May 12, 1994.

Bright, D.S., "Image Processing on the Macintosh: Free Software to Attach Practical Problems," Scientific Computing and Automation Conference and Exposition, Crystal City, Washington, October 13, 1993. Invited

Bright, D.S., "Image Processing and Database Tools," Air Force Technical Applications Center, Patrick AFB, Fl, NPP Technical Working Group Meeting, October 21, 1993. Invited

Bright, D.S., "Application of MacLispix, a Freeware Macintosh Image Processing Program, to the Analysis of X-ray Maps," Workshop on Advanced Materials, University of Sydney, Brisbane, Australia, February 5, 1994. Invited

Bright, D.S., "Image Processing Techniques with Applications to X-ray Maps and Other 2-Dimensional Micrographs," ACEM-13: Australian Society for Electron Microscopy, Inc., Gold Coast, Australia, February 10, 1994. Invited

Bright, D.S., "MacLispix and Other Image Processing Freeware for the Macintosh," ACEM-13: Australian Society for Electron Microscopy, Inc., Gold Coast, Australia, February 10, 1994. Invited

Bright, D.S., "Image Processing Techniques with Applications to X-ray Maps and Other 2-Dimensional Micrographs," weekly seminar, E.M. Facility, University of Sydney, Sydney, Australia, February 15, 1994. Invited

Bright, D.S., "The Application of MacLispix, a Free Macintosh Image Processing Program, to the Analysis of Micrographs," Mid-Atlantic Microbeam Analysis Society - Chesapeake Society for Microscopy Joint Meeting, NIST, April 7, 1994. Invited

Bright, D.S., "Image Processing Techniques, and Image Processing Freeware for the Macintosh Featuring MacLispix" Materials Reliability Division Seminar, NIST, Boulder, May 10, 1994. Invited

Bright, D.S., "Image Processing Techniques, and Image Processing Freeware for the Macintosh Featuring MacLispix," MAS tour speaker for CMAS Chapter meeting, Denver, CO, May 11, 1994. Invited

Bright, D.S., "MacLispix, a Free Macintosh Image Processing Program: Design Philosophy and Examples of Use," USGS Seminar, Denver, Colorado, May 11, 1994. Invited

Bright, D.S., "Analytical Imaging Techniques of the NIST Microanalysis Group: Survey, Applications and Digital Image Processing," Deauville Conference (2nd Symposium on

Analytical Sciences I, 13th International Symposium on Microchemical Techniques), Montreux, Switzerland, May 18, 1994. Invited

Bright, D.S., "Visibility of Objects in Noise: Computer Simulation and Test Results," Electron Microscopy Group Seminar, Cavendish Laboratory, University of Cambridge, England, May 25, 1994. Invited

Bright, D.S., "Visualization of Compositional Data in Microscopy: Representation Schemes and Software Tools," MSA-MAS Annual Meeting, New Orleans, August 2, 1994. Invited

Bright, D.S., Marinenko, R.B., and Bernik, S., "Identification of Multiphase Systems Using Compositional X-ray Maps," Microscopy Society of America-Microbeam Analysis Society 94 Meeting, New Orleans, LA, August 4, 1994.

Bright, D.S., "Basic Image Processing for the Microscopist: Practice and Pitfalls," 13th Annual Symposium on Advances in Microscopy, Duke U. Medical Center and N. C. Soc. for Microscopy and Microbeam Analysis, Wrightsville Beach, N.C., September 24, 1994. Invited

Bright, D.S., Workshop: "Use and Applications of NIH Image and MacLispix," 13th Annual Symposium on Advances in Microscopy, Duke U. Med. Center and N. C. Soc. for Microscopy and Microbeam Analysis, Wrightsville Beach NC, September 24, 1994. Invited

Bright, D.S., "Digital Image Processing with Mac Freeware: Illusions and Pitfalls," Mac User Group, National Gallery of Art, Washington, DC, September 20, 1994. Invited

Buntin, S.A., "Photodecomposition Dynamics of $Mo(CO)_6$/Si(111) 7x7," Adriatico Research Conference on Lasers in Surface Science, Trieste, Italy, August 10, 1994. Invited

Cavanagh, R.R., "Optical Heating of Surfaces: Time-Resolved Measurements of Adsorbate Vibrational Response," American Physical Society Meeting, Pittsburgh, PA, March 21, 1994. Invited

Cavanagh, R.R., "Optically Driven Surface Reactions: Laser Probes of Surface Dynamics," Department of Energy/Basic Energy Sciences Heterogeneous Catalysis and Surface Chemistry Research Conference, Oconomowoc, WI, May 25, 1994.

Cavanagh, R.R., "Ultrafast Time-Resolved Infrared Probing of Energy Transfer at Surfaces," Scandinavian Symposium on Infrared and Raman Spectroscopy, Bergen, Norway, June 1, 1994.

Chi, P.H., "Secondary Ion Mass Spectrometry Characterization of B- and Al-implanted α- and β-sic," 42nd ASMS Conference on Mass Spectrometry and Allied Topics, Chicago, IL, June 1, 1994.

Conny, J., "STD: What is it and Why is it Important in Surface Analysis," Surface Analysis '94 Conference, Burlington, MA, June 16, 1994.

Currie, L.A., "Total Quality Measurement and Chemical Technology," Perkin Elmer, Physical Electronics Division, Eden Prairie, MN, March 18, 1994. Invited

Currie, L.A., "The Revolution in Radiocarbon Dating: Its Impact on the Environmental Sciences," University of Maryland, College Park, MD, April 29, 1994. Invited

Currie, L.A., "Total Quality Measurement and Chemical Metrology," NIST Div. 834 Lunch Bunch, Gaithersburg, MD, May 17, 1994. Invited

Currie, L.A., "Total Quality Measurement: When the Customer's Needs Exceed the State-of-the-Art," General Motors R&D Facility, Warren, MI, June 7, 1994. Invited

Currie, L.A., "Univariate and Multivariate 'Test Pulses': An Introduction to Standard Test Data," Surface Analysis '94 MiniWorkshop on Standard Test Data, Burlington, MA, June 16, 1994.

Currie, L.A., "CIPM Interlaboratory Study 1: Impact of Reported Uncertainties," Meeting of the CIPM Working Group on Metrology in Chemistry, Gaithersburg, MD, July 5, 1994. Invited

Currie, L.A., "Proposal for a Small Sample Intercomparison," 15th International Radiocarbon Conference, Glasgow, Scotland, August 13, 1994. Invited

Currie, L.A., "Impact of the Chemical and Isotopic Blanks on the Interpretation of Environmental Radiocarbon Results," 15th International Radiocarbon Conference, Glasgow, Scotland, August 16, 1994.

Currie, L.A., "Individual Pulse Analysis: A Means for Characterizing Transient and Spurious Phenomena in Low-Level Counting," 15th International Radiocarbon Conference, Glasgow, Scotland, August 18, 1994.

Egelhoff, Jr., W.F., "Low Temperature Metal on Metal Epitaxy," American Physical Society Meeting, Pittsburgh, PA, March 22, 1994. Invited

Egelhoff, Jr., W.F., "Recent Progress in Research on the Giant Magnetoresistance Effect at NIST," National Storage Industry Consortium Quarterly Workshop, Boulder, CO, March 24, 1994.

Egelhoff, Jr., W.F., "Recent Studies of GMR Multilayers at NIST," National Storage Industry Consortium Annual Review Meeting, Monterey, CA, June 3, 1994.

Egelhoff, Jr., W.F., "XPS Forward Scattering: A Structural Diagnostic for Surfaces," University of Western Ontario, London, Ontario, Canada, June 24, 1994.

Etz, E.S., "Raman Microspectroscopy of Diamond and Diamond-Like Carbon Films," Symposium on Raman Microspectroscopy, XXth Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies (FACCS XX), Detroit, MI, October, 18, 1993. Invited

Etz, E.S., "New Data on CVD Diamond by Near-IR Excited FT-Raman Microspectroscopy," Workshop on Characterizing Diamond Films III, National Institute of Standards and Technology, Gaithersburg, MD, February 24, 1994.

Etz, E.S., "Improved Characterization of CVD Diamond by FT-Raman Spectroscopy," Symposium on Diamond and Related Materials, 1994 Spring Meeting of the Materials Research Society (MRS), San Francisco, CA, April 8, 1994.

Etz, E.S., "Molecular Compositional Analysis of High-Tech Materials by Fourier Transform Raman and Infrared Microspectroscopies," McClellan Central Laboratory, Technical Operations Division, McClellan AFB, Sacramento, CA, April 8, 1994. Invited

Etz, E.S., "Characterization of CVD Diamond by Fourier Transform Raman and Infrared Microspectroscopies," 1994 Joint Meeting of the Microscopy Society of America and the Microbeam Analysis Society, New Orleans, LA, August 2, 1994.

Fine, J., "The Scanning Scattering Microscope and Surface Microroughness Measurement," Fifth Topical Conference on Quantitative Surface Analysis, Clearwater Beach, FL, November 12, 1993.

Fine, J., "Collisional Deexcitation and Electron Transfer Processes at Ion Bombarded Surfaces," National Symposium of American Vacuum Society, Orlando, FL, November 15, 1993.

Fine, J., "Basic Radiation Damage Processes in Ionic Solids: The Role of Collisional Electron Capture," Materials Research Society Meeting, Boston, MA, December 1, 1993.

Fine, J., "Bombardment Induced Electronic Processes at Insulator Surfaces: The Role of Electron-Capture Collisions," Georgia Institute of Technology, School of Physics, Atlanta, GA, May 13, 1994. Invited

Fine, J., "Basic Radiation Damage Effects of Radiation on Materials," Sun Valley, ID, June 21, 1994.

Fine, J., "Collisional Electron Capture Processes at Ion Bombarded Insulator Surfaces," 10th International Workshop on Inelastic Ion Surface Collisions, Grand Targhee Resort, WY, August 8, 1994. Invited

Fine, J., "Formation of Autoionizing States by Electron-Capture Collisions," International Workshop on Auger Spectroscopy and Electronic Structure, Interdisciplinary Research Centre, University of Liverpool, UK, September 5, 1994.

Fine, J., "Electronic Transitions Due to Electron-Capture Collisions in Ion-Bombarded Molecular Compounds," 6th International Workshop on Desorption Induced by Electronic Transitions, Polonia Institute of the Jagellonian University, Krakow, Poland, September 27, 1994. Invited

Fine, J., "Bombardment Induced Electronic Processes at Insulator Surfaces: The Role of Electron-Capture Collisions," Particle Solid Interactions Conference, San Sebastian, Spain, September 28, 1994. Invited

Fletcher, R.A., "Elemental Images of Collected Atmospheric Particles by Secondary Ion Mass Spectrometry." Amer. Assoc. for Aerosol Research (AAAR) annual meeting. Oak Brook, IL, October 13, 1993.

Fletcher, R.A., "Selected Techniques for Chemical Characterization of Particles by Microanalysis," Pacific Northwest Lab (PNL), Pasco, WA, December 3-4, 1993. Invited

Fletcher, R.A.,"Laser Microprobe Analysis of Soot Precursor Particles," Amer. Assoc. for Aerosol Research. LA, CA, September 1, 1994.

Franzreb, K., "Collisional Electron Capture Processes at Ion-Bombarded Ionic Compound Surfaces," International Symposium on Surface Science, Savoie, France, March 10, 1994.

Gadzuk, J.W., "Surface Femtochemistry by Laser Excited Hot Electrons," Society of Photo-Optical Instrumentation Engineers, International Symposium of Lasers and Applications, Los Angeles, CA, January 24, 1994. Invited

Gadzuk, J.W., "The Coming of Age in Surface Dynamics: Beyond Statics to Femtoseconds," American Physical Society Meeting, Pittsburgh, PA, March 21, 1994. Invited

Gadzuk, J.W., "The Coming of Age in Surface Dynamics: Beyond Statics to Femtoseconds," 2nd European Conference on Gas-Surface Dynamics, Ambleside, England, September 6, 1994.

Germer, T.A., "Time-Resolved Infrared Probe of Substrate-Adsorbate Energy Transfer," Optical Society of America Meeting '93, Toronto, Canada, October 7, 1993.

Germer, T.A., "Time-Resolved Infrared Response of and Adsorbate to Visible and Ultraviolet Substrate Excitation," National Symposium of the American Vacuum Society, Orlando, FL, November 17, 1993.

Germer, T.A., "Excitation and Damping of Low Frequency Adsorbate Vibrations: The Role of Substrate Electrons and Phonons," Quantum Electronics and Molecular Physics Group, Harvard University, Cambridge, MA, December 9, 1993. Invited

Germer, T.A., "Ultrashort Laser-Induced Heating of Metals: An Adsorbate's Response," Department of Physics, Indiana University-Purdue University at Indianapolis, Indianapolis, IN, April 8, 1994. Invited

Germer, T.A., "Ultrashort Laser-Induced Heating of Metals: An Adsorbate's Response," Condensed Matter-Physics Group of the Department of Physics, Michigan State University, East Lansing, MI, April 11, 1994. Invited

Germer, T.A., "Excitation and Damping of Low Frequency Adsorbate Vibrations: The Role of Substrate Electrons and Phonons," American Physical Society April Meeting, Crystal City, VA, April 22, 1994. Invited

Gillen, G., "Macintosh-based Image Processing for Chemical Microscopy," Scientific Computing and Automation Conference, Washington, DC, October 13, 1993. Invited

Gillen, G., "Methods for Localization and Imaging of Human Brain Neurons Using SIMS," Secondary Ion Mass Spectrometry, SIMS 9, Yokohama, Japan, November 19, 1993.

Gillen, G., "High Spatial Resolution Isotope Ratio Imaging by SIMS," Annual Workshop on SIMS, Microelectronics Center of North Carolina, May 11, 1994.

Gillen, G., "Molecular Mapping of UV and Ion Beam Patterned Self Assembled Monolayer Films," Annual Workshop on SIMS, Microelectronics Center of North Carolina, May 11, 1994.

Gillen, G., "Recent Developments in Secondary Ion Microscopy," Microbeam Analysis Society Meeting, New Orleans, LA, August 1, 1994. Invited

Jach, T., "Physics of Magnetic X-Ray Scattering," Department of Physics, State University of New York at Albany, Albany, NY, October 7, 1993. Invited

Jach, T., "Surface Studies Using XPS and X-Ray Standing Waves at Grazing Angles," Department of Physics, State University of New York, Albany, NY, October 8, 1993. Invited

Jach, T., "Surface Studies Using Grazing Incidence XPS and Grazing Angle X-Ray Standing Waves," Surface Science Colloquium, Lawrence Berkeley Laboratory, Berkeley, CA, October 14, 1993. Invited

Jach, T., "Grazing Incidence XPS Studies of Oxidation on GaAs(100)," American Vacuum Society Meeting, Orlando, FL, November 15, 1993.

Jach, T., "Depth Dependence of Oxide Species in Oxidized GaAs as Determined by Grazing Incidence X-Ray Photoemission Spectroscopy," American Physical Society Meeting, Pittsburgh, PA, March 22, 1994.

Jach, T., "Grazing Incidence X-Ray Photoemission Spectroscopy: An Effective New Tool to Study the Depth Dependence of Chemical Species," Department of Physics, Murdoch University, Western Australia, May 13, 1994. Invited

Jach, T., "The NIST X-Ray Optical Bench for Evaluation of Optical Elements for Microfocussing," Workshop on Microanalysis, Sixth Users Meeting of the Advanced Photon Source, Argonne National Laboratory, Argonne, IL, May 26, 1994. Invited

Jach, T., "Grazing Incidence X-Ray Photoelectron Spectroscopy for the Study of Semiconductor Oxides," Westinghouse Advance Technology Laboratories, Baltimore, MD, August 4, 1994. Invited

Klouda, G., "Source Identification of Atmospheric Carbonaceous Aerosols and Gases via Radiocarbon Measurements: Applications to Urban Air Quality," International Atomic Agency, Vienna, Austria, December 2, 1993.

Klouda, G., "Progress Towards Validating the Separation of Atmospheric Volatile Organic Carbon from Air for ^{14}C Measurements," Measurement of Toxic and Related Air Pollutants Symposium, Durham, NC, May 5, 1994.

Klouda, G., "Radiocarbon Measurements of Wintertime Atmospheric Carbon Monoxide in Albuquerque, NM: Contributions of Residential Wood Combustion," Measurement of Toxic and Related Air Pollutants Symposium, Durham, NC, May 5, 1994.

Klouda, G., "Radiocarbon Measurements of Atmospheric Volatile Organic Compounds: Source Identification of Precursors to Ozone Formation," 15th International Radiocarbon Conference, Glasgow, Scotland, August 17, 1994.

Marinenko, R.B., "A Comparison of Electron Microprobe Data-Reduction Procedures for Thin Film Quantitative Analysis," 13th International Congress on Electron Microscopy, Paris, France, July 18-19, 1994.

Marinenko, R.B., "A Survey of Techniques Used by the Microanalysis Group at NIST," Institute Jozef Stefan University of Ljubljana, Ceramics Department, Ljubljana, Slovenia, July 26, 1994.

Marinenko, R.B., "Identification of Multiphase Systems Using Compositional X-Ray Maps," 1994 Joint Meetings of the Microscopy Society of America and the Microbeam Analysis Society, New Orleans, LA, August 4, 1994.

Myklebust, R.L., "Extracting Areas of Minor Peaks from Overlapped Spectra," 28th Microbeam Analysis Society, New Orleans, LA, August, 1994.

Newbury, D.E., "Desktop Spectrum Analyzer (DTSA): a Comprehensive Software Engine for Electron-Excited X-ray Spectrometry," Mid-Atlantic Microbeam Analysis Society, NIST, Gaithersburg, MD, November 1, 1993. Invited

Newbury, D.E., "Trace Nanoanalysis: Achieving High Sensitivity and High Spatial Resolution," Johns Hopkins University, Baltimore, MD, November 10, 1993. Invited

Newbury, D.E., "Trace Analysis of Nanoscale Materials by Analytical Electron Microscopy," Materials Research Society, Boston, MA, December 2, 1993. Invited

Newbury, D.E., "Microanalysis to Nanoanalysis," MSEL Reactor Radiation Division Seminar, National Institute of Standards and Technology, Gaithersburg, MD, January 11, 1994. Invited

Newbury, D.E., "Introduction to Electron Probe X-ray Microanalysis," Center for Interfacial Science, University of Minnesota, Minneapolis, MN, March 3, 1994. Invited

Newbury, D.E., "First Principles Spectrum Synthesis with DTSA," Center for Interfacial Science, University of Minnesota, Minneapolis, MN, March 3, 1994. Invited

Newbury, D.E., "'Standardless' Quantitative Analysis with DTSA," Center for Interfacial Science, University of Minnesota, Minneapolis, MN, March 4, 1994. Invited

Newbury, D.E., "Monte Carlo Modeling of Secondary Fluorescence at Phase Boundaries," Scanning 94 and the Southeast Electron Microscopy Society Annual Conference, Charleston, SC, May 17, 1994. Invited

Newbury, D.E., "Microbeam Analytical Techniques for Chemical Characterization of Nanometer-Scale Materials," Joint National Science Foundation-National Institute of Standards and Technology Conference on Ultrafine Particle Engineering, Arlington, VA, May 27, 1994. Invited

Newbury, D.E., "Basic Literacy in Electron Probe X-ray Microanalysis with Energy Dispersive X-ray Spectrometry: Qualitative and Quantitative Analysis," Joint Conference of the Microbeam Analysis Society and the Microscopy Society of America, New Orleans Convention Center, New Orleans, LA, August 2, 1994. Invited

Newbury, D.E., "Trace Nanoanalysis," Joint Conference of the Microbeam Analysis Society and the Microscopy Society of America, New Orleans Convention Center, New Orleans, LA, August 3, 1994. Invited

Newbury, D.E., "Electron Probe X-ray Microanalysis with Energy Dispersive X-ray Spectrometry: The Basics of X-ray Spectrum Interpretation," Joint Conference of the Microbeam Analysis Society and the Microscopy Society of America, New Orleans Convention Center, New Orleans, LA, August 3, 1994. Invited

Newbury, D.E., "Standardless Quantitative Electron Probe Microanalysis with Energy Dispersive X-ray Spectrometry: Is It Worth the Risk?" Joint Conference of the Microbeam Analysis Society and the Microscopy Society of America, New Orleans Convention Center, New Orleans, LA, August 5, 1994.

Newbury, D.E., "The Use of Simulated Standards in Quantitative Electron Probe Microanalysis with Energy Dispersive X-ray Spectrometry," Joint Conference of the Microbeam Analysis Society and the Microscopy Society of America, New Orleans Convention Center, New Orleans, LA, August 5, 1994.

Newbury, D.E., "Recent Developments in Microbeam Analysis at NIST," National Institute of Standards and Technology, Boulder, CO, September 19, 1994. Invited

Newbury, D.E., "Standardless Quantitative Electron Probe Microanalysis with Energy Dispersive X-ray Spectrometry: Is It Worth the Risk?" 13th Annual Symposium, Wilmington, North Carolina Society for Electron Microscopy and Microanalysis, Wilmington, NC, September 25, 1994. Invited

Powell, C.J., "The NIST X-Ray Photoelectron Spectroscopy Database," European Conference on Applications of Surface and Interface Analysis, Catania, Italy, October 5, 1993.

Powell, C.J., "Electron Inelastic Mean Free Paths for Organic and Other Low-Density Solids," Fifth Conference on Applications of Surface and Interface Analysis, Catania, Italy, October 6, 1993.

Powell, C.J., "Location of the Zero Point on the Binding-Energy Scale in X-Ray Photoelectron Spectroscopy," Fifth Topical Conference on Quantitative Surface Analysis, Clearwater Beach, FL, November 12, 1993.

Powell, C.J., "Electron Inelastic Mean Free Paths for Organic and other Low-Density Solids," National Symposium of American Vacuum Society, Orlando, FL, November 15, 1993.

Powell, C.J., "Development of Standard Test Data for Surface Analysis," Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie, MN, March 18, 1994. Invited

Powell, C.J., "International Development of Standards for Surface Analysis and ISO 9000," SEMATECH Materials and Bulk Processes Metrology Workshop, Austin, TX, May 5, 1994. Invited

Powell, C.J., "Elastic-Electron-Scattering Effects on Angular Distributions in X-Ray Photoelectron Spectroscopy," Surface Analysis '94 Conference, Burlington, MA, June 16, 1994.

Powell, C.J., "Elastic-Electron-Scattering Effects on Angular Distributions in X-Ray Photoelectron Spectroscopy," Gordon Research Conference on Electron Spectroscopy, Henniker, NH, July 6, 1994.

Powell, C.J., "Cross Sections and Inelastic Processes for Auger-Electron Spectroscopy and X-Ray Photoelectron Spectroscopy," Eighth International Conference on Quantitative Surface Analysis, Guildford, England, August 24, 1994. Invited

Powell, C.J., "Elemental Binding Energies for X-Ray Photoelectron Spectroscopy," Eighth International Conference on Quantitative Surface Analysis, Guildford, UK, August 25, 1994.

Powell, C.J., "Activities of ISO Technical Committee 201 on Surface Chemical Analysis," Eighth International Conference on Quantitative Surface Analysis, Guildford, UK, August 26, 1994.

Powell, C.J., "Inelastic Electron-Scattering Processes Relevant to Quantitative Auger-Electron Spectroscopy," Physics Department, University of York, York, England, August 30, 1994. Invited

Powell, C.J., "Formation of Autoionizing States by Electron-Capture Collisions," Third International Workshop on Auger Spectroscopy and Electronic Structure," Liverpool University, Liverpool, UK, September 6, 1994.

Powell, C.J., "Calibration of the Kinetic-Energy Scale on Auger-Electron Spectrometers," Third International Workshop on Auger Spectroscopy and Electronic Structure, Liverpool University, Liverpool, UK, September 6, 1994.

Powell, C.J., "Improvements in the Precision and Accuracy of Surface Analyses by Auger-Electron Spectroscopy and X-Ray Photoelectron Spectroscopy," short course at Eighth Latin American Congress on Surface Science and its Applications, Cancun, Mexico, September 18-22, 1994. Invited

Powell, C.J., "Effects of Elastic and Inelastic Electron Scattering on Quantitative Surface Analysis by Auger-Electron Spectroscopy and X-Ray Photoelectron Spectroscopy," Eighth Latin American Congress on Surface Science and its Applications, Cancun, Mexico, September 19, 1994. Invited

Richter, L.J., "External Reflection FTIR Spectroscopy Investigation of the Thermal and Photochemistry of $Mo(CO)_6$ Adsorbed on Si(111) 7x7 at 100 K," National Symposium of the American Vacuum Society, Chicago, IL, November 13, 1993.

Richter, L.J., "Nonlinear Optical Studies of Buried $Si/CoFi_2$ Interfaces," American Physical Society Meeting, Pittsburgh, PA, March 22, 1994.

Richter, L.J., "Nonlinear Optical Studies of Semiconductor Interfaces," Adriatico Research Conference on Lasers in Surface Science," Trieste, Italy, August 11, 1994. Invited

Robey, S.W., "Surface Structure and Composition of Oxide Substrate Materials: The Influence of Surface Preparation," National Symposium of the American Vacuum Society, November 17, 1993.

Robey, S.W., "Photoemission Study of the Transition from Correlated Metal to Mott-Hubbard Insulator in $Nd_xSr_{1-x}TiO_3$," American Physical Society Meeting, Pittsburgh, PA, March 22, 1994.

Simons, D.S., "Secondary Ion Imaging of STM-Modified Semiconductor Surfaces," Ninth International Conference on Secondary Ion Mass Spectrometry, Yokohama, Japan, November 10, 1993.

Simons, D.S., "Quantification in SIMS - Some Success Stories," Ninth International Conference on Secondary Ion Mass Spectrometry, Yokohama, Japan, November 11, 1993. Invited

Simons, D.S., "The Development of Standard Reference Material 2137 - A Boron Implant in Silicon Standard for Secondary Ion Mass Spectrometry," Microbeam Analysis Society, New Orleans, LA, August 3, 1994.

Simons, D.S., "How Quantitative is Dynamic SIMS Analysis of Semiconductors?" International Conference on Quantitative Surface Analysis QSA-8, Guildford, UK, August 25, 1994. Invited

Small, J.A., "Automated Scanning Electron Microscopy of Particles, Scanning Meeting, Charleston, SC, May 18, 1994. Invited

Small, J.A., "The Prompt-Gamma Activation Analysis of Particles Excited by a Focused Neutron Probe," Microbeam Analysis Society, New Orleans, LA, August 2, 1994.

Steel, E.B., "Quality Assurance and the Analytical Laboratory," AFTAC NPP Meeting, Patrick Air Force Base, Florida, October 6, 1993. Invited

Steel, E.B., "X-ray Focussing for Analytical Chemistry," AFTAC NPP Meeting, Patrick Air Force Base, Florida, October 6, 1993. Invited

Steel, E.B., "A Thin Film Standard for Analytical Electron Microscopy," AFTAC NPP Meeting, Patrick Air Force Base, Florida, October 7, 1993. Invited

Steel, E.B., "Characterization of Particles: Microanalysis," Annual Meeting of American Association for Aerosol Research, Oak Brook, IL, October 11, 1993.

Steel, E.B., "Historical Perspective of Proficiency Testing of Asbestos Laboratory Accreditation," National Voluntary Accreditation Program Regional Meeting, Chicago, IL, July 22, 1994. Invited

Steel, E.B., "Quality Assurance in Microanalysis: ISO 9000, Guide 25, et al." Microbeam Analysis Society Annual Meeting, New Orleans, LA, August 4, 1994.

Steel, E.B., "Historical Perspective of Proficiency Testing of Asbestos Laboratory Accreditation," National Voluntary Accreditation Program Regional Meeting, Gaithersburg, MD, August 24, 1994. Invited

Velapoldi, R.A., "Measurements for Non-Proliferation," Interagency R&D Subcommittee Meeting, DoE, Forrestal Bldg., Washington, D.C., December 3, 1993. Invited

Velapoldi, R.A., "Overview of Division 837," Lincoln Labs, Boston, MA, April 12, 1994.

Velapoldi, R.A., "Overview of NIST/CSTL," University of VA, Gaithersburg, MD, August 5, 1994.

Verkouteren, R.M., "Development of Isotopic Standards for Atmospheric Research: Issues and Progress at NIST," IAEA Consultants' Group Meeting on Stable Isotope Standards and Intercalibration, Vienna, Austria, December 2, 1993. Invited

Verkouteren, R.M., "Production of Isotopic Gas Standards: Issues and Progress at NIST," 1994 National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory Annual Meeting, Boulder, CO, March 9, 1994.

Verkouteren, R.M., "Batch Production of Microchemical AMS Targets: Methods and Measurements for Radiocarbon," 15th International Radiocarbon Conference, Glasgow, Scotland, August 18, 1994. Invited

Verkouteren, R.M., "Evaluation of Fe-C Bead Target Chemistry: Reduction Rates, Yield and Isotopic Fractionation," 15th International Radiocarbon Conference, Glasgow, Scotland, August 18, 1994.

Wight, S.A., Small, J.A., and Bright, D.S., "Development of an Automated Scanning Electron Microscope Test Sample," American Association of Aerosol Research Annual Meeting, Oak Brook, IL, October 13, 1994.

Wight, S.A. and Small, J.A., "Design and Construction of a Multiple Take-Off Angle EDS Detector," Joint Meeting of the Microscopy Society of America and the Microbeam Analysis Society, New Orleans, LA, August 2, 1994.

Wight, S., Fletcher, R., and Bryner, N., "Analysis of Desert Aerosol By Environmental Scanning Electron Microscope and Laser Microprobe Mass Spectrometer," Fourth International Aerosol Conference, Los Angeles, CA, August 30, 1994.

Winkler, D.C., "Inner-Shell Electron-Excitation in the Methylmethoxysilanes," Sigma Xi Post-Doctoral Poster Presentation, NIST, Gaithersburg, MD, February 24, 1994.

Zeissler, C.J., "VRD: Practical Applications", Patrick Air Force Base, Florida, October 1994.

Zeissler, C.J., "Sample Preparation for Particle Analysis," Microbeam Analysis Society Chuck Memorial Tour, Mid Atlantic Microbeam Analysis Society, NIST, Gaithersburg, MD, April 7, 1994. Invited

Zeissler, C.J., "Sample Preparation for Particle Analysis," Microbeam Analysis Society Chuck Memorial Tour, Midwest Microbeam Analysis Society, Lansing MI, April 20, 1994. Invited

Zeissler, C.J., "Sample Preparation for Particle Analysis," Microbeam Analysis Society Chuck Memorial Tour, New Mexico Microbeam Analysis Society, Albuquerque, NM, June 16, 1994. Invited

3. Cooperative Research and Development Agreements (CRADAs) and Consortia

Precise Measurement Methodologies for Determining Particle Size Distribution Using Optical Particle Counters, R.A. Fletcher
HIAC/ROYCO (CRADA)

EPMA/SEM Automated Mapping Utilizing DTSA, R.L. Myklebust
4pi Analysis, Inc. (CRADA)

Chemical Microstructural Characterization by Microbeam Analysis, D. Newbury
American Superconductor Corporation (CRADA)

The Characterization of X-ray Optical Elements, T. Jach
X-Ray Optical Systems (CRADA)

Ion Assisted Deposition of Ceramic Films, S.W. Robey
Science Applications International Corporation (CRADA)

Deposition and Characterization of SrS Thin Films, T.-J. Hsieh
Optex Communication Corporation (CRADA)

4. Patent Awards and Applications

Jach, T. and Thurgate, S., "X-ray Photoelectron Emission Spectrometry System," Patent No. 5,280,176 (Issued January 1994)

Fiori, C.E. (deceased) and Swyt, C.R., "Desktop Analyzer, A Computer Program to Analyze Spectra," Patent No. 5,299,138 (Issued March 1994)

5. SRMs

SRM 1867	Uncommon Commercial Asbestos
SRM 1868	Quantitative Asbestos in Building Materials
SRM 2064	Thin Film Glass (in progress)
SRM 2135	Ni/Cr Multilayer (in progress)

6. SRD Activities

SRD 20	X-Ray Photoelectron Spectroscopy (New Version)
SRD 36	NIST/NIH Desktop Spectrum Analyzer, Release 2.0.1

Ion Sputter Yields (in progress)

7. Calibrations

Calibration of Ozone Photometers:

- Environment Canada, AQB
- Environmental Protection Agency - SRP7
- IN USA, Inc.
- Ministry of Environment and Energy
- National Oceanic and Atmospheric Administration
- NIST - SRPO
- TBV Science (United Kingdom)
- Xerox Corporation

8. Committee Assignments

D.S. Bright

- EMSA/MAS File Standards Committee

R.R. Cavanagh

- Laser Surface Interactions Conference (Co-chair)
- Gordon Research Conference on Dynamics at Surfaces (Chair)

L.A. Currie

- DoD (AFTAC), RPP Panel
- CIPM Working Group on Chemical Metrology
- IUPAC Commission V.1 (General Aspects of Analytical Chemistry)
- IUPAC Working Group on Chemometrics
- IUPAC Commission on Environmental Analytical Chemistry
- IUPAC Analytical Chemistry Division Committee
- NSF Advisory Board for WHOI Accelerator Laboratory (Chairman)
- Organizing Committee: 1995 Chemometrics Conference

E.S. Etz

- ASTM E-13 Molecular Spectroscopy
- ASTM E-13.08 Raman Spectroscopy

J. Fine

- Sub-committee on Standard Reference Materials, ASTM Committee E-42 on Surface Analysis (Chairman)

R.A. Fletcher

National Fluid Power Association Contamination Committee, T2.9
IES Working Group 014 - Calibration of Airborne Particle Counters
American Association of Aerosol Research Working Group - Aerosol Chemistry

J.W. Gadzuk

International Advisory Committee, 7th International Conference on Vibrations at Surfaces

G.Gillen

ASTM E-42.06 Secondary Ion Mass Spectrometry

T. Jach

SEMATECH - Analytical Laboratory Manager's Working Group
American Physical Society - Sorting Committee

R.L. Myklebust

ASTM E-42.96 ISO TC/202/TAG on Microbeam Analysis (Chairman)

D.E. Newbury

American Society for Testing and Materials: Surface Analysis, E-42
Microscopy Society of America: Standards Committee

C.J. Powell

ASTM Committee E-42 on Surface Analysis (Member of Executive Committee, International Liaison, Member of US Technical Advisory Group for ISO/TC 201 on Surface chemical Analysis, Member of Subcommittee E-42.03 on Auger Electron Spectroscopy, Member of Subcommittee E-42.04 on X-Ray Photoelectron Spectroscopy, and Chairman of Task Group on Energy-Scale Calibrations)
Technical Committee 201 on Surface Chemical Analysis of the International Organization for Standardization (Chairman)
Surface Chemical Analysis Technical Working Area, Versailles Project on Advanced Materials and Standards (US representative and Vice-Chairman)
Applied Surface Science Division, International Union of Vacuum Science, Technique and Applications (US representative and Vice-Chairman)
International Program Committee, Thirteenth International Vacuum Congress and Ninth International Conference on Solid Surfaces
Organizing Committee, Fifth and Sixth Topical Conferences on Quantitative Surface Analysis (Chairman)
International Program Committee and Advisory Board, Third International Workshop on Auger Spectroscopy and Electronic Structure
International Scientific Advisory Committee, Sixth European Conference on Applied Surface and Interface Analysis
International Scientific Committee, International Workshop on Auger-Electron Spectroscopy-From Physics to Data

D.S. Simons

ASTM E-42 Surface Analysis
ASTM E42.06 Secondary Ion Mass Spectrometry
ASTM E42.09 Standard Reference Materials
ISO TC201 Surface Chemical Analysis - SC6 Secondary Ion Mass Spectrometry
Microbeam Analysis Society (Secretary)

J.A. Small

Microbeam Analysis Society - President
ASTM D-22 Sampling and Analysis of Atmospheres

E.B. Steel

ASTM D-22 Sampling and Analysis of Atmospheres

R.M. Verkouteren

IAEA Consultants' Working Group on Isotopic Data Reduction Procedures

R.A. Velapoldi

ASTM E-11 on Statistical Methods
ASTM E-13 on Molecular Spectroscopy
ASTM E-13.06 on Molecular Luminescence
ASTM E-13.06.01 on Presentation of Corrected Fluorescence Spectra
ASTM E-13.06.02 on Recommended Practices on Molecular Fluorescence Spectroscopy
DoE Review Committee
Interagency Research and Development Subcommittee, Nonproliferation Center
Federal Interagency Task Force on Air Pollution Research

S. A. Wight

Microbeam Analysis Society, Membership Services (Chair)
American Association for Aerosol Research, Instrumentation Working Group (Chair)

9. Editorships

D.S. Bright

Journal of Computer Assisted Microscopy (Editorial Board)
Microanalysis Journal (Editorial Board)

L.A. Currie

CRC Press Chemometrics Series (Advisory Editor)

E.S. Etz

Microbeam Analysis Journal (Editorial Board)

J.W. Gadzuk

Progress in Surface Science (Advisory Editorial Board)

D.E. Newbury

Journal of Microscopy (Editorial Review Board)
Scanning (Editorial Review Board)
Journal of Trace and Microprobe Techniques (Editorial Review Board)
Microbeam Analysis (Editorial Review Board)

C.J. Powell

Applied Surface Science (Editorial Board)
Surface and Interface Analysis (Editorial Board)
Methods of Surface Characterization (Editorial Board)
Journal of Electron Spectroscopy and Related Phenomena (Editorial Board)
Surface Science Spectra (Editorial Board)
Journal of Vacuum Science and Technology A (Associate Editor)

10. Seminars

October 25, 1993

David S. Bright, NIST, "MacLispix and Other Image Processing Freeware for the Macintosh Applied to Micrographs." (Division Sponsor: R.A. Velapoldi)

October 26, 1993

Z. Sroubek, Academy of Sciences of The Czech Republic, Prague, Czech Republic, "Secondary Ion Emission from Insulator and Semiconductor Surfaces." (Division Sponsor: J. Fine)

November 4, 1993

Ian Harrison, University of Virginia, Charlottesville, VA, "Reaction Dynamics on Surfaces." (Division Sponsor: S.A. Buntin)

November 9, 1993

Douglas Doren, University of Delaware, Newark, DE, "Theory of Elementary Reactions on Solid Surfaces." (Division Sponsor: R.R. Cavanagh)

November 19, 1993

Bengt Kasemo, Chalmers University of Technology, Goteborg, Sweden, "Potassium on Graphite: Structure, Vibrational Excitations, Photodesorption, and Intercalation Kinetics." (Division Sponsor: J.W. Gadzuk)

November 29, 1993

Steven D. Brown, University of Delaware, Newark, DE, "Nonlinear Calibration, Modeling and Classifications Using Feedforward Neural Networks Trained with Adaptive, Quasi-Newton Optimizers." (Division Sponsor: L.A. Currie)

December 21, 1993

R.D. Misra, University of Pennsylvania, Philadelphia, PA, "Interactions Among Trace and Alloying Elements at Interfaces in Metallic Alloys and their Relevance to Materials Properties." (Division Sponsor: W.F. Egelhoff)

January 10, 1994

Tony H. Ha, University of Central Florida, Orlando, FL, "Surface Acoustic Wave Charge Transport Devices." (Division Sponsor: W.F. Egelhoff)

March 22, 1994

Siegfried Hofmann, Max-Planck-Institut fur Metallforschung, Stuttgart, Germany, "Recent Progress in High-Resolution Depth Profiling." (Division Sponsor: C.J. Powell)

April 18, 1994

Abdul Mesarwi, Physics Department, University of Houston, Houston, TX, "Growth and Characterization of Multilayer Superconductors and Superconductor/Ferroelectric Heterostructures for Device Applications." (Division Sponsor: W.F. Egelhoff, Jr.)

May 26, 1994

Jack Judy, University of Minnesota, Minneapolis, MN, "Magnetic Information Technology." (Division Sponsor: W.F. Egelhoff)

June 15, 1994

Roger Tobin, Michigan State University, Department of Physics and Astronomy, Lansing, MI, "Surface Resistivity Probed with Broadband Infrared Reflectance." (Division Sponsor: R.R. Cavanagh)

July 12, 1994

Lars Osterlund and Dinko Chakarov, Chalmers University of Technology, Goteborg, Sweden, "Thermal and Photon-Stimulated Interactions of Oxygen and Water Coadsorbates with Potassium on Graphite." (Division Sponsor: R.R. Cavanagh)

July 27, 1994

Paul Geladi, Dept. of Organic Chemistry, University of Umeâ, Sweden, “Multivariate Image Regression - Methods, Visualization, and Chemical Examples.” (Division Sponsor: D.S. Bright)

September 2, 1994

Dennis Masson, Chemistry Department, University of California, San Diego, CA, "State Selective Detection of the Photodissociation and Photodesorption of N_2O-Pt(111)." (Division Sponsor: R.R. Cavanagh)

11. Conferences/Workshops/Sessions Sponsored/Co-Sponsored

November 12-13, 1993
Fifth Topical Conference on Quantitative Surface Analysis, Clearwater Beach, FL (C.J. Powell)

March 3-4, 1994
"Desktop Spectrum Analyzer (DTSA): A Comprehensive Introduction," Dept. of Chemical and Materials Engineering, University of Minnesota, Minneapolis, MN (D.E. Newbury, R.L. Myklebust, C.R. Swyt)

May 10-12, 1994
Seventh Annual Workshop on Secondary Ion Mass Spectrometry, Microelectronics Center of North Carolina, Raleigh-Durham, NC (G. Gillen)

May 17-18, 1994
Workshop on Monte Carlo Techniques for Scanning Electron Microscopy and Microanalysis, Scanning 94 and the Southeast Electron Microscopy Society Conference, Charleston, SC (M. Postek and D.E. Newbury)

June 16, 1994
Mini-Workshop on the Development of Standard Test Data for Surface Analysis, Burlington, MA (C.J. Powell, L.A. Currie, and J. Conny)

August 3, 1994
Session on "Standardization of Microscopy and Microanalysis Under ISO Protocols: MSA and MAS Responsibilities and Opportunities" Joint Conference of the Microbeam Analysis Society and the Microscopy Society of America, New Orleans, LA (E.B. Steel and D.E. Newbury, co-organizers)

August 9-12, 1994
Adriatico Research Conference on Lasers in Surface Science, International Center for Theoretical Physics, Trieste, Italy (R.R. Cavanagh, Co-Chair)

September 19, 1994
NIST Multilaboratory Strategic Planning Workshop on Nanotechnology, Boulder, CO (R.A. Velapoldi, Organizing Committee Member)

September 24, 1994
"Desktop Spectrum Analyzer (DTSA): An Overview of Principal Functions", 13th Annual Symposium, North Carolina Society for Electron Microscopy and Microanalysis, Wrightsville Beach, NC (D.E. Newbury and R.L. Myklebust)

12. Other

a. Software Development

D.S. Bright

MacLispix, a public domain image processing package for the Macintosh.

b. Faculty Appointment

D.E. Newbury

Adjunct Professor, Dept. of Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania

VII. Thermophysics Division

Richard F. Kayser, Chief

A. Division Overview

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, and pressure, vacuum, partial pressure, and leak rate. 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.

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 provision 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 alternative 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 physicochemical data and models needed to develop more robust and species-specific separation processes.

Accurate **pressure, vacuum, and leak-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 leak rate. The pursuit of these goals requires in-depth investigations of pressure and vacuum instrumentation, including piston gages, ultrasonic interferometer manometers, capacitance diaphragm gages, ionization gages, spinning rotor gages, and partial pressure analyzers. The Division provides calibration services for pressure and vacuum (from 10^{-7} to 10^{9} Pa) and for leak rate (from 10^{-14} to 10^{-5} mol/s) and offers precision measurement workshops in these areas.

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 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 38 pure refrigerants and mixtures with as many as five components. To date, the NIST Standard Reference Data Program has distributed more than 400 copies of REFPROP, and the Air Conditioning and Refrigeration Institute and the Electric Power Research Institute have adopted REFPROP as the source of thermophysical properties data for their Alternative Refrigerants Evaluation Program. Future efforts in the area of alternative refrigerants will concentrate on the identification and characterization of alternatives for 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 on the properties of **advanced working fluids**. This is an area in which accurate and comprehensive thermophysical properties are essential to design and optimize the performance of power plants and refrigeration systems. New programs in this area are focusing on ammonia-water mixtures as alternatives to water as the working fluid in power cycles, and on mixtures of noble gases as possible working fluids in large-scale thermoacoustic refrigerators. Recent developments indicate that ammonia-water mixtures promise significantly improved energy efficiencies 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. The objectives of several projects are to provide the natural gas industry and the rate payer with the validated property data and models needed for 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 within the Division. In a related project, the Gas Processors Association has supported measurements 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 elucidating the behavior of trace contaminants, such as halogenated hydrocarbons, in natural gas distribution systems, and work on standardizing the chemical analysis of natural gas mixtures, especially for components consisting of more than six carbon atoms.

The **development of new experimental apparatus** to study industrially important fluids and fluid mixtures is a vital component of the overall program on thermophysical properties. 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 with inserts 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, low- and high-pressure ebulliometers, re-entrant radio-frequency resonator for detecting phase transitions non-visually), and dielectric properties (concentric-cylinder dielectric-constant apparatus). 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 **Fluid Properties Data Center** comprises another set of major activities for the Division. 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 predicting 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 modeling work on aqueous systems. For example, the Data Center and the Process Measurements Division are collaborating on a long-term project on the **hydrothermal processing** of hazardous and toxic wastes. This technology exploits the fact that a wide variety of materials can be hydrolyzed and oxidized to mostly innocuous products under the relatively mild conditions of water near its critical point. An overall goal is to develop comprehensive models for the properties and phase behavior of multicomponent aqueous mixtures containing salts, CO_2, air components, and organic and inorganic compounds.

Based on numerous industrial interactions, meetings, and workshops, the Division has identified several promising new directions in the area of thermophysical properties. In the area of **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 interactions with organizations such as the Design Institute for Physical Properties Data (DIPPR). The aim of the program on **Dilute Solutions** will be 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. These results will have a major impact on the design and optimization of processes for removing 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 **inter**molecular (condensed-phase) properties via the incorporation of quantum mechanical force and energy calculations into molecular dynamics and Monte Carlo simulation codes. Finally, the goals of the program on **Semiconductor Gases** will be to develop and use novel acoustic techniques to measure the equilibrium and transport properties of the 50 or so gases important in 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 industrial processes based on **supercritical fluid extraction** (SFE). The best candidates for SFE are high-cost, low-volume chemicals, such as natural products, that require the use of nontoxic solvents. Although carbon dioxide is the classical supercritical fluid solvent, the Division has begun to focus more heavily on the use of alternative refrigerants as supercritical fluid solvents. These fluids offer a polar, yet pure alternative to carbon dioxide with and without polar additives. Much of the other research focuses on **environmental separations**, which is appropriate given the emphasis within the chemical and related industries on environmental concerns, and in particular, on waste minimization and pollution prevention. In the area of **membrane separations**, there are currently two projects, one aimed at using membranes as "molecular filters" to selectively permeate combustion products (CO_2 and H_2O) from a fluidized-bed waste incinerator while retaining other species, and one aimed at separating H_2S from natural gas. Long-term goals in this area are to understand the relationship between the membrane casting process and the microstructure of the membrane and between the microstructure and properties of the membrane and its separation characteristics. Another area of significant interest is **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 regeneration.

Recent advances in **pressure and vacuum** range from the development of **new standards and calibration services** to significant **improvements in instrumentation**. In the range near and above atmospheric pressure, the Division is engaged in a very promising 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 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 uncertainty of its Ultrasonic Interferometer Manometers (NIST's most accurate primary pressure standards) 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. Another noteworthy accomplishment was the completion of a new flow standard for generating water vapor at pressures from 10^{-5} to 10^{-1} Pa; water is a ubiquitous contaminant in vacuum systems, and quantitative measurements are crucial in the processing of advanced materials (see below). 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 undoubtedly broaden the use of that technology significantly for a variety of applications, including process control.

Based on information collected through industrial interactions, roadmaps, meetings, and workshops, the Division has initiated several new programs 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 programs 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 on developing **improved end-use instrumentation**. Inasmuch as water is the most prevalent contaminant in vacuum systems, a statement reinforced by the outcome of a three-day workshop, the Division is focusing its near-term efforts on the measurement of low-density water vapor. The partial pressures of interest, 10^{-8} to 10^{-1} Pa, are between 0.1 parts per trillion and 1 part per million of atmospheric pressure. With regard to end-use instrumentation, the Division plans to extend its original studies of Residual Gas or Partial Pressure Analyzers (RGAs or PPAs) to elucidate the fundamental causes of their metrological deficiencies and to identify possible solutions. It is also 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. A third major program in the semiconductor area involves the development and dissemination of **new standards for low flow rates** to address the needs of the semiconductor industry in the important range between 0.1 and 100 standard cm^3/min. A collaboration with the Process Measurements Division, this program will cover a variety of gases and include studies of the performance of thermal mass flow controllers, which are widely used throughout the industry.

FY94 was an excellent year from the point of view of recognition. Dr. Michael R. Moldover was elected a Fellow of the American Physical Society for his pioneering research in low-temperature physics, critical phenomena, interfacial phenomena, and acoustic metrology. Dr. J.M.H. (Anneke) Levelt Sengers was named an Honorary Fellow of the International Association for the Properties of Water and Steam. Dr. Levelt Sengers, Dr. William M. (Mickey) Haynes, Mr. Laurell R. Phillips, Ms. Becky A. Stevenson, and Ms. Carol A. Thomas were commended by the American Society of Mechanical Engineers for their outstanding contributions to the 12th Symposium on Thermophysical Properties. Dr. Haynes was honored with the Department of Commerce Silver Medal for his outstanding leadership and technical contributions to the world's preeminent research program on the properties of industrially important fluids. Dr. Richard A. Perkins was recognized with the Department of Commerce Bronze Medal for developing state-of-the-art techniques for measuring the thermal conductivity of highly polar and electrically conducting fluids. Dr. Mark O. McLinden and Ms. Stephanie L. Outcalt were selected for a NIST Measurement Service Award for their outstanding contributions to the NIST Standard Reference Data Program in the area of high-accuracy equations of state for alternative refrigerants, and Dr. Archie P. Miiller was selected for a NIST Measurement Service Award for his extraordinary contributions and improvements to the calibration of low-pressure gages. Dr. Rosemary A. MacDonald was honored for her outstanding service to the NIST Chapter of Sigma Xi.

The Thermophysics Division consists of five groups, Properties of Fluids and Process Separations, located in Boulder, CO, and Fluid Science, Pressure, and Vacuum, located in Gaithersburg, MD. The following Technical Reports describe the activities and major accomplishments of these groups in more detail.

B. Selected Technical Reports
(Thermophysics Division)

1. The Twelfth Symposium on Thermophysical Properties

J.M.H. Levelt Sengers and W.M. Haynes

The Twelfth Symposium on Thermophysical Properties was held on the campus of the University of Colorado at Boulder from June 19-24, 1994. This Symposium, which continues the series started in 1959, was organized by the Thermophysical Properties Committee of the ASME Heat Transfer Division. NIST staff members Anneke Levelt Sengers and Ared Cezairliyan (Metallurgy Division) played key roles in organizing the technical program of the conference. W.M. Haynes was responsible for the local organization and will chair the Thirteenth Symposium in 1997.

The Symposium, which convenes every three years, represents the premier international conference concerned with the theoretical, experimental, and applied aspects of the thermophysical properties of gases, liquids, and solids. More than 80 percent of the papers dealt with fluid properties. The conference attracted 400 participants from industry, academia, and government laboratories from 35 countries who contributed almost 400 papers. The number of participants represented an increase of more than 30 percent from the previous conference. On the basis of the number and quality of papers and on the interactions generated among the participants, the conference was a tremendous success. Special sessions on refrigerant properties, natural gas properties, structure of fluids, fluid systems under shear, molecular simulation, acoustic techniques, supercritical fluids, databases and data correlation, and properties in low gravity were organized by members of the Thermophysics Division; these sessions were characterized by papers of the highest technical quality that represented the latest developments in these areas. The special sessions were extremely well attended and received by the participants.

Welcoming remarks at the opening session were given by Dr. David Norcross, Director of the NIST-Boulder Laboratories. The keynote address was given by Dr. Graham R. Mitchell, Assistant Secretary for Technology Policy, Technology Administration, U.S. Department of Commerce; his talk was entitled "Building a Technology Base to Fuel the New American Economy." The plenary lecture, "Thermophysical Properties: What Have We Learned Recently, and What Do We Still Need to Know?", was delivered by Professor Stanley I. Sandler of the University of Delaware. The Twelfth Symposium was also the forum to present the Yeram S. Touloukian Award to Professor Joseph Kestin (posthumously), Brown University and to Dr. Guy White, CSIRO, Lindfield, Australia for their distinguished contributions to the study of thermophysical properties.

2. Thermodynamic Properties of Alternative Refrigerants

J.W. Magee, M.O. McLinden, L.A. Weber, D.R. Defibaugh, C.D. Holcomb, K.A. Gillis, S.L. Outcalt, J.W. Schmidt, M.L. Huber, M.R. Moldover, J.S. Gallagher, J.B. Howley, and W.M. Haynes

The Thermophysics Division has been involved with refrigerants for nearly 15 years. The early work was in conjunction with studies of refrigerant mixtures in heat pumps by the NIST Building Environment Division. With the more recent concerns about ozone depletion caused by the CFC (chlorofluorocarbon) and HCFC (hydrochlorofluorocarbon) refrigerants, the Division's work has evolved into a comprehensive, world-class program to study and characterize a wide variety of alternative refrigerants. The Division's activities consist of experimental measurements, compilation of literature data, correlation of data, and theoretical modeling studies. Accurate values of the thermodynamic properties are vital to evaluate the performance (energy efficiency, capacity, etc.) of a new fluid in refrigeration applications and to design refrigeration equipment using the alternative refrigerants.

During the past year, the Division completed comprehensive measurements of the thermodynamic properties of R143a and selected measurements on R152a, which were combined with literature data to yield a comprehensive data set. These two fluids are constituents of mixtures which are leading candidates to replace HCFC-22. The measurements included vapor pressure, pressure-volume-temperature (PVT) behavior, isochoric heat capacity, speed of sound, surface tension, and the triple point and critical point parameters; the measurements covered very wide ranges of temperature and pressure in the liquid, vapor, and supercritical states. The new measurements for R143a and R152a, together with literature data, were used to fit standard-reference-quality modified Benedict-Webb-Rubin (MBWR) equations of state that are valid from near the triple point to over 400 K. These equations were developed using a multiproperty 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. Earlier MBWR equations of state for R123, R32, and R125 were also updated to include new data.

Not all potential refrigerants warrant comprehensive measurements. Thus, limited data were obtained for R245ca and R236fa; these data consist of vapor pressure, liquid density, and vapor-phase sound speed and PVT measurements over a temperature range of roughly 0 to 100 °C, along with critical point determinations. These data allow a preliminary assessment of a potential refrigerant.

Refrigerant mixtures are becoming increasingly important as alternative refrigerants, particularly as replacements for HCFC-22. Comprehensive measurements including PVT, heat capacity, and vapor-liquid equilibrium (VLE) have been completed for the R32/134a mixture; similar measurements for the R32/125 system are in progress. In addition to being leading candidates to replace HCFC-22, these mixtures were selected for study and the experimental measurements were designed to yield the data most useful in developing mixture models.

Version 4 of the REFPROP refrigerant properties database was released by the NIST Standard Reference Data Program during 1994. Major enhancements included the addition of 12 new fluids, high-accuracy MBWR formulations for 10 additional fluids, and experimentally determined mixing parameters for additional mixtures. The 12 new fluids included several of the "natural refrigerants," i.e., ammonia, carbon dioxide, and four hydrocarbons.

3. Transport Properties of Alternative Refrigerants

R.A. Perkins, A.R. Laesecke, J.B. Howley, M.L. Huber, D.C. Ripple (836), L. Cusco (Imperial College, London, U.K.), K. Meier (Universität Hannover, Germany), M.L.V. Ramires (Universidade de Lisboa, Portugal), A. Gurova (Instituto Superior Technico, Portugal), and C.A. Nieto de Castro (Universidade de Lisboa, Portugal)

The measurement and correlation of transport properties for alternative refrigerants are complementary to the study of their equilibrium thermodynamic properties, and the Thermophysics Division has a comprehensive program to measure, correlate, and predict both thermal conductivity and viscosity. These properties are required to determine the size of refrigeration equipment and the efficiency of foam insulation manufactured using alternative refrigerants.

During the past year, comprehensive measurements of the thermal conductivity and viscosity of R32, R134a (see also the following report), R152a, R143a, and R236ea were completed in the liquid, vapor, and supercritical gas phases. Thermal conductivity measurements were also completed for the R32/R125 azeotropic mixture, and for the R32/R125 equimolar mixture in the liquid, vapor, and supercritical gas phases; saturated liquid viscosity measurements were performed on R32, R152a, and R143a from 255 to 323 K. Of course, the correlation and prediction of the transport properties of alternative refrigerants is our final product. Based on data measured in the Thermophysics Division and obtained from the literature, correlations have been developed for many alternative refrigerants, incorporating theory where possible. In the case of thermal conductivity, a very significant critical enhancement has been observed that can be modeled quite well with mode-coupling crossover theory. Extended-corresponding-states approaches also are being developed to correlate measured transport properties and to predict the transport properties for proposed alternative refrigerants, including mixtures, when no data are available.

4. International Activities on CFC Alternatives

M.O. McLinden, R.A. Perkins, and W.M. Haynes

During the past year, the Thermophysics Division continued to serve as "operating agent" (coordinator) for a project entitled "Thermophysical Properties of the Environmentally Acceptable Refrigerants" under the auspices of the International Energy Agency (IEA). The objectives of this project, initiated in 1990 and known as Annex 18, are (a) 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 (b) to determine (including experimental measurements and the evaluation and correlation of data) the thermophysical properties of these fluids leading to the publication of comprehensive, internationally accepted properties bulletins. At present, Canada, Germany, Japan, Norway, Sweden, the United Kingdom, and the United States are members of the Annex. In addition to NIST, the United States is represented by Texas A&M University, the University of Idaho, and the Colorado School of Mines. In 1993, the Annex was renewed for a second three-year term; this second phase is concerned with replacements for R22 and other HCFC (hydrochlorofluorocarbon) refrigerants, with a focus on refrigerant mixtures and "natural refrigerants" such as ammonia and the simple hydrocarbons. A comprehensive comparison of refrigerant mixture models has been initiated during this second phase. In this task, modeling groups have been invited to submit their models for comparison against a database of experimental mixture property data. The evaluation process will focus on two reference mixtures, R32/125 and R32/134a. In other tasks, equations of state for the properties of pure R32 and pure R125 will be evaluated, and an assessment of the state of the art for the thermodynamic and transport properties of ammonia will be prepared.

The Division is participating in the third United Nations Environment Programme technical reassessment associated with the Montreal Protocol on Substances that Deplete the Ozone Layer, the international treaty that regulates the production of CFCs and HCFCs. This process was initiated in 1993 and will provide input for the renegotiation of the phase-out timetable and other provisions of the Protocol in 1995. M.O. McLinden is serving on the panel responsible for the "Technical Options Report" on refrigeration and air-conditioning; during the past year, he was the lead author of the "Refrigerant Data" section of this report.

In addition, the Division is an active participant in IUPAC (International Union of Pure and Applied Chemistry) work on the transport properties of alternative refrigerants. Inasmuch as the highly polar HFC (hydrofluorocarbon) and HCFC refrigerants present special difficulties for some of the standard techniques for measuring thermal conductivity and viscosity, NIST has organized an international round-robin test series which is currently underway on a "standard" refrigerant, R134a. This round-robin test will assess the accuracy of transport property data measured on a well characterized sample using various independent techniques at NIST (U.S.), Imperial College (U.K.), Sheffield University (U.K.), Universidade de Lisboa (Portugal), Aristotle University (Greece), Keio University (Japan), Technical University of Munich (Germany), and University of Rostock (Germany). The first results from these round-robin tests were presented at the 12th Symposium on Thermophysical Properties in Boulder in June 1994. The Division also hosted the meeting of the IUPAC Transport Properties Subcommittee in conjunction with the 12th Symposium.

5. Chemical Analysis Procedures for Alternative Refrigerants

T.J. Bruno, M. Caciari (Fort Lupton High School, Ft. Lupton, CO), and K.H. Wertz (University of Colorado)

The calculation of reliable and accurate thermophysical properties for alternative refrigerant fluids depends upon measurements that are performed on well-characterized fluid samples. A major focus of the Division's research program on alternative refrigerants has therefore been the development of the needed chemical analysis technology to thoroughly characterize the purity of research samples. Our efforts in this direction have included the development of analytical methods and sample handling procedures, the design and construction of novel instrumentation, and the compilation of a comprehensive database of analytical data. The database contains information for fluid analysis by gas chromatography, mass spectrometry, infrared and ultraviolet-visible spectrophotometry, nuclear magnetic resonance spectrometry (using ^{1}H, ^{13}C, ^{19}F, and ^{17}O nuclei), and refractometry, in addition to physical property data that are useful for handling and identification.

The major focus of our research during the last year has been the measurement and analysis of gas chromatographic retention parameters of alternative refrigerants and their potential impurities and reaction products. We have completed measurements of net retention volumes and relative retentions of methane-, ethane-, ethene-, propane-, propene-, propyne-, and ether-based fluids on a stationary phase that is particularly useful: a 5% coating of a low-molecular-mass polymer of hexafluoropropylene epoxide on a graphitized carbon black. In the near future, we plan to measure the response factors of thermal conductivity detectors; these data will form the basis of an automated identification and quantitation system based on chromatographic characteristics.

6. Thermophysical Properties of Natural-Gas Mixtures

J.W. Magee, C.D. Holcomb, D.G. Friend, W.M. Haynes, and L.J. Van Poolen (Calvin College)

The Thermophysics Division has been engaged in a comprehensive experimental and theoretical research program for two decades to provide the natural gas industry and the rate payer with the validated property data needed for custody-transfer transactions, for energy optimization in gas industry operations, and for the design and control of gas processes.

During the past year, density measurements have been carried out on natural-gas-liquid components and mixtures as part of a project sponsored by the Gas Processors Association (GPA). The purpose of this work was 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. The experimental work has been performed at NIST, while much of the modeling has been done at the Colorado School of Mines. Saturated liquid (and vapor) density measurements have been carried out on propane, normal butane, normal pentane, isopentane, and isohexane at temperatures from 240 to 420 K. Single-phase pressure-density-temperature measurements have been carried out on two binary mixtures of ethane and propane and one 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. This project has resulted in a reduction by a factor of two (0.5 percent) in the uncertainty of the properties involved in the custody transfer of natural gas liquids; a 0.5 percent uncertainty corresponds to an inequity of more than $3 million on a monthly basis.

In a related project, revisions have been made to the NIST Mixture Property Program to make it more useful to gas industry users, including a major liquid-natural-gas distributor. The NIST Mixture Property Program is a Standard Reference Database that provides accurate thermophysical property calculations for natural gas components and mixtures based on an extended corresponding states algorithm. The improvements included a revised user interface, additional options, and a revision of certain default conditions to facilitate use in the field. Further refinements will be implemented in the next general release planned for 1995, including additional options for tables, additional choices of properties to be calculated, and elimination of discontinuities in calculated properties.

7. Separation of Trace Contaminants from Natural Gas

T.J. Bruno, J.E. Mayrath, and R. Einert (University of Colorado)

Natural gas is a complex, two-phase (gas and liquid) mixture of organic and inorganic constituents, most of which are naturally occurring, some of which are introduced intentionally during processing. The gas phase consists of approximately 40 major constituents and 175 minor constituents, while the liquid phase can contain between 350 to 450 compounds. While some of the constituents are of environmental concern, it is important to have an understanding of all families of compounds present to ensure efficient gas industry operations.

In previous years, the Division has concentrated on the separation of trace levels of heavy halogenated organics such as polychlorinated biphenyls (PCB's) from natural gas. This year, our focus has been to provide a thorough characterization of the C_6+ hydrocarbon fraction to facilitate and standardize a gas chromatographic procedure known as the extended natural gas analysis. The extended natural gas analysis is the basis for many important energy-design calculations such as calorific value. Unfortunately, explicit account is not taken at present of the hundreds of compounds that have more than six carbon atoms.

The specific objectives of the current project are to measure temperature programmed retention indices of representative compounds (from the 175 in the C_6+ fraction of the gas phase) on a number of important capillary-column stationary phases, and ultimately, to develop an expert system to design and control such analyses. This predictive routine, based on measured data, would allow standardization of the extended natural gas analysis throughout the gas industry. During the past year, a comprehensive literature search was completed that identified all known natural gas constituents, both natural and anthropogenic. Moreover, the physical properties relevant to the design of chromatographic analyses were compiled into a database; in addition to providing on-line access to these properties, this database also performs important chromatographic calculations for four carrier gases: helium, hydrogen, nitrogen, and argon. The current measurements of retention indices will be used to develop the database into a predictive chromatographic design tool.

8. Measurement of the Thermal Properties of Electrically Conducting Fluids Using Coated Transient Hot Wires

R.A. Perkins, J.B. Howley, A.R. Laesecke, M.L.V. Ramires (Universidade de Lisboa, Portugal), and C.A. Nieto de Castro (Universidade de Lisboa, Portugal)

The transient hot-wire technique is a fast, accurate, and reliable method for measuring the thermal conductivity and thermal diffusivity of fluids. Normally, bare hot wires immersed in the fluid of interest are used simultaneously as electrical heat sources and as resistance thermometers; however, electrical conduction through the fluid can be a significant problem for highly polar fluids. This problem can be avoided by electrically insulating the hot wires from the fluid; for example, anodization has been described in the literature as an efficient way to electrically insulate tantalum hot wires while producing only very thin (70 nm) surface films.

A new transient hot-wire cell using anodized tantalum hot wires was completed this year for use in electrically conducting fluids. This new cell is constructed of a nickel alloy for good corrosion resistance in aqueous systems with halide salts. The tantalum hot-wire cell has been demonstrated to operate reliably from 300 to 550 K at pressures to 70 MPa. Prior to work at NIST, this anodized wire technique had been demonstrated only for the liquid phase. During the past year, measurements have been made in the liquid, vapor, and supercritical gas phases of a number of polar and nonpolar fluids with anodized 25 μm diameter tantalum hot wires. The results agree well with thermal conductivity measurements made with other techniques and with NIST work on relatively nonpolar materials using bare platinum hot wires; the measurements on nonpolar fluids include argon gas from 300 to 340 K and 0.1 to 70 MPa, and liquid toluene from 300 to 550 K. The measurements on polar fluids include R134a from 300 to 450 K, R152a from 300 to 410 K, and R143a from 300 to 375 K. All of these polar fluids were measured in the liquid, vapor, and supercritical gas phases at pressures to 70 MPa. Measurements will be made in the near future on water, ammonia, and ammonia/water mixtures using the tantalum hot-wire cell.

As described above, the tantalum hot-wire cell has been shown to work reliably for thermal conductivity measurements in the liquid, vapor, and supercritical gas phases using the standard transient mode of operation. However, in the dilute vapor (< 1 MPa), corrections for the finite wire dimensions become large for the 25 μm diameter tantalum hot wires. We have shown that it is possible to avoid this problem by operating the wires in a steady-state mode. In fact, the steady-state results obtained for argon, R134a, R152a, and R143a at pressures below 1 MPa using the anodized tantalum hot-wire cell agree quite well with transient results using the same cell and with results from other laboratories using a variety of techniques. Thus, NIST has developed the capability to measure the thermal conductivity of electrically conducting liquids, vapors, and supercritical gases from 300 to 550 K using anodized tantalum hot wires in either a transient or steady-state mode.

9. Acoustic Resonators with Inserts for Measuring the Transport Properties of Gases

K.A. Gillis and M.R. Moldover

During previous years, we developed very-low-loss acoustic resonance techniques to optimize the accuracy of speed-of-sound measurements in gases, and our techniques have been adopted by laboratories around the world. During the past year, we have designed and tested two new classes of resonators.

Resonators in one class have two cavities connected by a capillary tube, and their resonances have large viscous losses resulting from the acoustic flow of the test gas in the capillary. The comparatively simple geometry of these resonators allows them to be used as absolute viscometers, i.e., they yield the viscosity from dimensional and frequency measurements alone. Moreover, their all metal construction makes them suitable for viscosity measurements under severe conditions, e.g., at high temperatures and/or with corrosive gases.

Resonators in the second class have an insert with a large surface area near their center. A typical insert is an array of parallel plates. Depending upon the resonance mode, these resonators will have large losses resulting from either the viscosity or the thermal conductivity of the test gas; the gas motion near the insert causes the losses for the various modes. These resonators are well suited for measuring the Prandtl number [i.e., the ratio (viscosity)/(density × thermal diffusivity)] of the test gas under difficult conditions. The Prandtl number is a key parameter governing heat transfer from a solid to a flowing fluid.

10. *Ab Initio* Calculations for Helium as a Standard for Gaseous Transport Property Measurements

M.R. Moldover

Traditionally, accurate measurements of the viscosity and thermal conductivity of helium have been combined with measurements of the second virial coefficient to determine the parameters in ever-more-refined models for the helium-helium interatomic potential. In contrast, after many years of effort, very accurate quantum mechanical calculations of the ground state potential have become available. These *ab initio* results have been fitted by model potentials that had no experimental input.

During the past year, we have found that the best *ab initio* model potentials are able to predict the "standard" ^{3}He and ^{4}He virial coefficients and transport properties with significantly smaller deviations than any of the earlier "experimental" or model potentials. Indeed, it appears that the uncertainty in calculated properties is less than that of the best measurements. The *ab initio* potential also reproduces both the total and the differential ^{4}He-^{4}He scattering cross section data as well as or better than the semi-empirical potentials that have been used in the past.

Based on these observations, we now recommend reversing the traditional practice and using the *ab initio* results to calibrate apparatus for measuring the transport properties of gases. This change will reduce the uncertainty of helium-based gas thermometry and the uncertainty in the measured transport properties of more complex gases. The *ab initio* results also resolve a controversy about the quality of data from different laboratories, and they circumvent the unfortunate circumstance that the most accurate, albeit delicate, viscometer for gases near ambient temperature is no longer in operation.

11. Models for the Critical Region of Mixtures Based on Scaling Laws

J.C. Rainwater

Many important chemical processes occur in mixtures near critical conditions. Some of these include supercritical extraction with carbon dioxide (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 from the critical pressure to about three-fourths of that pressure.

The Leung-Griffiths model, as modified by Moldover and Rainwater, has been designed by us specifically for the critical region of mixtures and explicitly incorporates nonclassical critical exponents. During the past several years, the model has provided highly accurate critical-region vapor-liquid equilibrium (VLE) correlations for 45 nonazeotropic and 25 azeotropic binary mixtures. These include almost all mixtures that have been thoroughly measured in 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 some difficulty correlating thermodynamic variables other than pressure, temperature, composition, and density; however, entropies and enthalpies have been examined with a generalized Clausius-Clapeyron equation, and work is in progress to determine chemical potentials by means of a critical-region thermodynamic consistency test. Certain simplified asymptotic equations have been derived and tested for limited regions of the phase diagram, such as the case of a dilute nonvolatile solute in a supercritical volatile solvent, and some theoretical questions concerning the critical locus have been clarified.

The present emphasis is to extend the model to a Type 2 mixture with both VLE and liquid-liquid equilibrium (LLE). All phase boundaries and the three-phase liquid-liquid-vapor locus are to be described by nonclassical exponents, and no spurious phase boundaries can appear. A successful generic model has been constructed during the past year, and efforts are in progress to adjust the model parameters to provide accurate fits of actual mixture phase equilibrium data. The first mixture to be examined is carbon dioxide + methane, which does not directly exhibit LLE. However, there is convincing evidence that, when cooled, this mixture would undergo liquid-liquid separation except that it freezes first. Subsequently, mixtures with actual LLE data in the proximity of VLE will be examined; examples are carbon dioxide + carbon disulfide, water + sulfur dioxide, and hydrogen + neon. A long-term project is to construct along similar lines a model of a Type 3 mixture with a discontinuous critical locus; this represents the extreme limit of immiscibility. Most aqueous mixtures are Type 3, as are mixtures of carbon dioxide with compounds whose molecules contain two or more carbon rings, such as tetralin or trans-decalin.

12. Static Dielectric Constant of Water and Steam

D.P. Fernández (Comision Nacional de Energia Atomica, Argentina), A.R.H. Goodwin (University of Idaho), J.M.H. Levelt Sengers, and Y. Mulev (National Polytechnic Academy, Belarus)

The static dielectric constant of water, including steam and supercritical high-pressure, high-temperature states, is an indicator of the electrolytic character of the aqueous medium, and governs the types of chemistry that may occur under varying conditions. With the new interest in hydrothermal reactions for destroying hazardous materials and synthesizing new compounds, the temperature and pressure ranges of hydrothermal applications have expanded, as has the variety of chemical reactions being studied in supercritical states over a large range of density. The dielectric constant of water and steam and its pressure and temperature derivatives also enter into formulations of the standard states and thermodynamic properties of electrolyte solutions.

During the past year, the Thermophysics Division, with the co-sponsorship of the International Association for the Properties of Water and Steam (IAPWS), has been leading a project to characterize the static dielectric constant of water and steam, including supercritical states, on the ITS-90 scale, and over the full range of available data. The project has had several aspects: (a) collection of the entire data base, mostly contained in unpublished theses, transformation to ITS-90, and critical evaluation; (b) inclusion of recent, as yet unpublished, data in the steam phase, obtained at the Moscow Power Institute; (c) new measurements of the dielectric constant of liquid water at NIST, to elucidate a discrepancy involving earlier NBS data; and (d) development of a new formulation incorporating the ITS-90-based equation of state for water and steam being prepared under the auspices of IAPWS. Manuscripts reporting the results of (a) and (c) have been completed, and a new formulation for the dielectric constant is near completion. The new formulation will receive a final touch when the ITS-90 based IAPWS equation of state is finalized, which is expected to happen within the next few months. A report on the project was presented in September 1994 at the 12th International Conference on the Properties of Water and Steam and has been submitted for publication in the Proceedings.

13. Thermodynamic Properties of Ammonia-Water Mixtures

D.G. Friend, J.C. Rainwater, M.L. Huber, C.D. Holcomb, J.W. Magee, R.A. Perkins, A. Olson (University of Colorado), and L.J. Van Poolen (Calvin College)

Fluid mixtures of ammonia and water have been identified as important working fluids in a variety of novel power generation technologies as well as in refrigeration cycles. A pilot cogeneration plant based on this binary system has been operational, and studies indicate that dramatic improvements in efficiencies may be feasible. A basic component of the design exploits the variation of the bubble point temperature with composition; this enables the development of highly efficient heat exchange processes prior to the gas expansion stage which drives the conventional turbine. The private sector has been supportive of this technology, and licensing agreements with a major industrial manufacturer are in place. However, capital costs associated with power generation facilities are high, and it is necessary to optimize plant design and to develop warranty criteria for turbine manufacturers and plant fabricators.

For the above reasons, and despite an abundance of data and approximate thermophysical property surfaces for the mixture, it is necessary to develop an independent, accurate, evaluated, and widely accepted standard for the thermophysical properties of the ammonia-water system. Toward this end, during the past year we have collected more than 9700 experimental data from the archival literature, theses, reports, etc., and converted them to a consistent set of units in a standard electronic format. In addition, we have completed a study of the critical-region vapor-liquid equilibrium (VLE) surface based on a scaling-theory model and have identified the most promising sets of data, from among inconsistent sets, to model the critical line and VLE surface in the critical region, and to extrapolate to lower pressures. An extended corresponding states (ECS) predictive model has been shown to give generally reasonable results, although the liquid region is not adequately described. A more accurate ECS model, using exact pure-fluid shape factors constructed from the standard reference equations of state for water and ammonia, has been implemented. Preliminary results indicate that this model should be able to describe the mixture thermodynamic surface quite well, although the current version with only two adjustable parameters may have to be revised.

During the coming year, the experimental program on the ammonia + water system will begin. Limited measurements will be conducted to better define the VLE surface and to obtain mixture densities, heat capacities, and thermal conductivities. The ECS model will be further optimized as the data acquisition and evaluation process continues. A computer package, which will define the interim thermodynamic surface, will be completed for testing and limited distribution.

14. Properties of Aqueous Mixtures at High Temperatures and Pressures

J.M.H. Levelt Sengers, D.G. Friend, J.S. Gallagher, and J.A. Given (831)

The technology of supercritical water oxidation (SCWO), in which oxidizing chemical reactions can be used to decompose and detoxify various organic and inorganic hazardous materials, provides a primary motivation for studying mixtures of water and atmospheric gases (carbon dioxide, nitrogen, and oxygen) in the temperature region 500 to 700 K with pressures to 300 MPa. In particular, accurate thermophysical properties, especially phase equilibria, are key to developing and exploiting these methods. The binary systems of interest are considered to be Type 3 in a common classification scheme, according to the topography of the critical surfaces. These are systems in which the constituents are very dissimilar and the pure fluid critical points are widely separated. Type 3 systems have a discontinuous critical line between the two pure critical points, and the high temperature branch of the curve can have complex behavior and extend to very high pressures.

We have previously used a generalized corresponding states model to successfully describe the thermodynamic surface of the CO_2-H_2O system, but were less successful for the N_2-H_2O system because the components are even more dissimilar. During the past year, we studied a different version of the extended corresponding states model in which each pure fluid is described by a very accurate standard-reference-quality thermodynamic surface, and only two additional parameters are used to define mixture properties; this model is similar to that used in the NIST Mixture Property Program, but the standard water surface recommended by the International Association for the Properties of Water and Steam (IAPWS) and a method to locate critical lines have been incorporated into the program. However, although the method can give a reasonable description of the mixture thermodynamic surface, it fails to model the critical region topology accurately and it cannot represent existing data to within the experimental uncertainties.

We will consider several modifications and alternative approaches in the next phase of these studies. It remains to be seen whether a more recent water thermodynamic surface, an alternative reference fluid, or additional adjustable parameters to improve the description in the critical region could improve the model. It may be necessary to explore fundamentally different approaches that account more directly for hydrogen-bonding effects.

15. Molecular Dynamics Simulations of Polarizable Water

R.D. Mountain and W.J. Stevens (831)

Molecular dynamics simulation of liquids and solids at the molecular level has become an important tool for theoretical studies. This is particularly true for aqueous systems where the complexity of the liquid environment can be probed directly via simulations. Because the usefulness of a simulation depends on the extent that the interactions model employed represents the important physical features of the fluid, it is important to pay close attention to the details of the molecular interactions.

The utility of explicitly including molecular-polarizability-based interactions in molecular dynamics simulations of water and aqueous solutions is a major topic of current interest. The large dielectric constant of water is due to polarization-based interactions. Including polarizability in the energy relations makes it possible to include changing local environments in a systematic way, but at the cost of significantly increased computational requirements. This is because polarization results in many-body interactions instead of pairwise-additive interactions obtained with conventional models.

We are taking a two-part approach to addressing this issue. The first part is to develop a detailed molecular model that includes polarization. This model is based on *ab initio* quantum chemistry calculations of the water dimer. This is work in progress that will enable us to evaluate the value of various levels of complexity in interaction models. The second part is to use molecular dynamics simulations to determine the site-site pair distributions of water at several thermodynamic states using a fixed-charge (nonpolarizable) interaction model and using a relatively simple model that includes polarizability. These studies provide a preliminary indication of the costs and benefits of including polarizability. The results of these simulations are being compared with experimentally derived site-site pair distribution functions. These quantities are now available for normal conditions of density and temperature ($\rho = 997$ kg/m^3, T = 300 °C), and at elevated temperatures ($\rho = 720$ kg/m^3, T = 300 °C; and $\rho = 660$ kg/m^3, T = 400 °C, the last state being in the supercritical region). Initial results indicate that the polarizable model follows the experimentally found trends with increasing temperature and decreasing density more closely than do the results of the nonpolarizable model. The cost is that the polarizable model requires about three times as much computational effort as the nonpolarizable model.

The results of these simulations will guide the development of our polarizable model. When it is developed, we will evaluate the costs and benefits associated with the use of realistic polarizable models in molecular dynamics simulations in an aqueous environment and apply them to several interesting research areas such as ions in supercritical water and biomolecules in solution.

16. Neutron Scattering Studies of the Structure of Complex Fluids

H.J.M. Hanley, G.C. Straty, B.D. Butler, S.H. Sinha (Exxon), C.D. Muzny (University of Colorado), F. Tsvetkov (Solar Dynamics, Israel), D. Pfeiffer (Exxon), and M.Y. Lin (Exxon)

This program investigates the relationship between the properties of a liquid and its microscopic structure. The properties of a liquid are obtained from the appropriate integrals of the pair correlation function or its Fourier transform, the structure factor. Many of the studies involve measuring the structure factor by neutron scattering, and we have made extensive use of the SANS (small angle neutron scattering) spectrometers at the NIST Cold Neutron Research Facility. We are particularly interested in the behavior and properties of fluids under unusual experimental conditions, e.g., near a phase transition, in a gelation environment, or under the influence of an external field, such as shear.

Currently, we are emphasizing (1) the study of systems containing a mix of inorganic and organic components, and applying the results to such apparently diverse areas as pollution remediation and the development of nanometer composite materials, (2) the study of the structure of mixtures of hydrocarbons that are nonideal (that is, mixtures that have a finite heat of mixing and an excess volume), and (3) apparatus development, including the construction of a light scattering facility and a significant upgrade of the Couette shearing cell used at the NIST SANS facility. Highlights for this year include the following:

(i) A study of the phenomenon of gelation based on SANS data from an aqueous silica gels included the variation of the gel structure as a function of volume fraction, and in particular, the variation of the range of scattering wavevectors over which the gel is fractal. The results indicated for the first time that an applied shear has a substantial influence on the rate of gelation and on the final gel structure. Moreover, computer simulations have indicated possible strong connections between the gelation mechanism and the phenomena of spinodal decomposition and nucleation of a simple fluid; these connections are under further study.

(ii) An investigation (together with scientists from Exxon) of the properties of worm-like micelles. Initially spherical at very low surfactant concentrations, the micelles 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 conventional polymers, however, the worms break and reform continuously; thus, the solution is stable when subjected to an extremely high mechanical stress, and its properties recover when the stress is removed. During the past year, we have clarified the shapes and growth patterns of the micelles using SANS for the solution under shear and light scattering for the solution at rest. We plan to use similar techniques to investigate other types of micellar systems, including mixtures of micelles and clay minerals.

17. Supercritical Fluid Extraction of Pharmaceuticals and Metals

T.J. Bruno, B.N. Hansen, and A.F. Lagalante (University of Colorado)

With the advent of the Montreal Protocol's chlorofluorocarbon (CFC) production phaseout, many of the chlorinated liquid solvents used for cleaning and extraction processes are also being phased out. This circumstance, combined with the fact that the most commonly used supercritical fluid solvent, carbon dioxide, has a very low solvent strength, have led us to study some of the most promising fluorinated alternative refrigerants for use as solvents in liquid and supercritical fluid extraction. Many of these fluids are gases under ambient conditions (R32, R22, R124, R125, R116, R134a, R143a) with properties that are well suited to supercritical fluid extraction processes. The tunable solvent strength of a supercritical fluid offers the potential of selective extraction, followed by depressurization and collection of the extract with the pure gaseous solvent ready for re-use.

Pharmaceuticals that are not sufficiently soluble in supercritical fluid carbon dioxide have been studied in alternative refrigerants and carbon dioxide/micelle systems. In recent years, the Division has measured the solubility of taxol (an anticancer drug), capsaicin (a drug used for the treatment of shingles, a common complication of AIDS), dipalmitoylphosphatidylcholine (used in the treatment of infant respiratory distress syndrome), and β-carotene (an anti-oxidant and precursor of vitamin A) in alternative refrigerants and micelle systems. Modeling with equations of state and solubility parameters has also been done. The predicted solubility, pressure, and temperature can be used to select the most promising solvent and physical conditions for an extraction process before measurements are made.

In addition to the work on pharmaceuticals, we have done extensive solubility measurements of metal-β-diketonate complexes in carbon dioxide. These systems are of great interest to support and optimize wastewater cleanup and metal ore extraction processes. During the past year, pressure-temperature-solubility surfaces have been measured and modeled for variations in β-diketonate ligand and central metal atom in the molecule.

Future plans include the continued development and application of property measurement technology and the development of a unified solubility model based on physical and chemical properties.

18. Gas Sorption in Polymers for Separation

J.J. Pellegrino, M.R. Yetzbacher, and B.R. Mattes (Los Alamos National Laboratory)

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 transport properties of mixtures in particular polymers. This project addresses the collection of quality data for the sorption of gases and vapors in industrially-significant polymers and for the development of quantitative structure/property prediction methods.

During the past year, two experimental apparatus have been built using conventional pressure-decay methodology, and data have been obtained for the sorption of O_2, N_2, and Ar in the conducting polymer polyaniline. A thermodynamic solubility model based on a modified Flory-Huggins approach has been used to correlate the results in terms of two physical parameters. The next phase of the project will include gas sorption measurements on meta-substituted polysulfones, in addition to further studies on polyaniline. Work with these particular polymers will provide a means to vary both chemical and structural subgroups in the polymer, which will be critical to develop techniques to predict transport properties, and ultimately, to delineate rational design criteria for separations.

19. Adsorptive Separation Techniques and Fundamental Data

J.E. Mayrath and L.A. Watts

Adsorption techniques are attractive alternatives to precipitation, evaporation, and distillation for the cleanup of dilute waste streams, and also in some gas separations. Adsorption columns are relatively insensitive to process upsets, and require only some form of breakthrough detection and switching valves for effective process control. The practical information necessary to develop and apply a given adsorption process includes adsorbent capacity, regenerability, lifetime under regeneration conditions, and cost. In addition, the adsorption process is very sensitive to the particle density, size, porosity, and surface area. Some processes require knowledge of selective adsorption interactions between a species of interest and adsorbents suitable for the separation; many of these parameters are related to fundamental quantities that are both theoretically and experimentally accessible.

During the past year, we have completed a review of novel low-cost adsorbents suitable for the removal of heavy metal ions from dilute aqueous waste streams. The review includes the practical economic and engineering constraints that would be applied to real process development. Adsorbents surveyed included a wide variety of natural products and industrial refuse or scrap materials. These materials are of interest because they are inexpensive and a high adsorption capacity is unnecessary for many applications. A more general literature survey is currently underway to review the more fundamental aspects of adsorption, including mathematical models and measurements of selective adsorption from mixtures. This work will result in recommended models and measurement protocols for developing an improved understanding of the basic principles of adsorption processes for separation.

20. Numerical Modeling of Separation Processes

G.R. Hardin and A.P. Peskin

Packed-columns are used in many industrially important separation processes, such as distillation, adsorption, and chromatography. Generally, 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. To address problems such as these, we have been developing a general-purpose capability for rate-based modeling of momentum, heat, and mass transfer with homogeneous and heterogeneous chemical reactions.

During the past year, we have been working on numerical fluid dynamics techniques to model the relative motion of systems of particles and a fluid; we are incorporating these techniques into our transport-phenomena software library. Also included in our software is the ability to model moving boundaries, such as surface growth with shape change, and moving free surfaces. Our long-term goal is to create the necessary tools and knowledge base to enable improved process designs.

Our most recent work has been focusing on the electrochemical cleanup of dilute mixed-waste streams. Dilute effluent streams are problematic because separation processes must "fight" equilibrium to remove more of an already dilute pollutant. We are examining moving-bed electrodes as a basis for devices to process large volumes of dilute pollutants. These devices have unique problems resulting from the flow of current through the bed; particles tend to agglomerate, creating dead zones, one of the major packed-bed problems mentioned above. We are applying our recently installed numerical techniques for modeling particle flow to study the interaction of electrically-conducting moving particles in an electric field to elucidate the physics governing this problem. Next year, we will begin to apply these techniques to the study of flow distribution and channeling in packed beds for other separation processes, such as adsorption.

21. Measurement Services for Pressure, Vacuum, and Leak Rate

P.J. Abbott, S.W. Doty, R.G. Driver, C.D. Ehrlich, A.R. Filippelli, R.W. Hyland, C.R. Tilford, S.A. Tison, and D.B. Ward

The Thermophysics Division provides calibration and special test services to a wide range of aerospace, defense, instrumentation, process, and utility industries over extended ranges of pressure and flow (leak rate). Piston gage standards are maintained between 10^4 and 10^9 Pa, mercury manometer and orifice-flow vacuum standards are maintained between 10^{-7} and 10^6 Pa, and constant-pressure flow standards cover the range 10^{-14} to 10^{-4} mol/s.

Division calibration activities during the past year were comparable to previous years. Calibration of piston gages decreased from 56 to 23, but the calibration of low-pressure gages (predominantly capacitance diaphragm gages) increased from 24 to 32 and leaks increased from 12 to 18. The increase in workload for the vacuum (low-pressure) service was actually larger than indicated by these figures. A large number (15) of capacitance diaphragm gages, not included in the above figures, were calibrated to support reduced uncertainties and range extension for the flow standards, and three different high and ultra high vacuum transfer standards were calibrated as part of an international round robin. This year also marked the first full-year of use of the Transition Range vacuum standard, which was used in part for the calibration of low-range capacitance diaphragm gages, helping to relieve the increased load on that service. In the interest of efficiency and cost-containment, it has been the practice to do vacuum calibrations in two batches a year for each type of instrument, but customer demand and the needs of the flow standards program required semi-continuous calibrations of capacitance diaphragm gages. At the same time, significant gains were made in the data analysis and report preparation procedures for this program; these improvements will help us deal effectively in the future with surges in calibration workload.

22. Development of Very-Large-Diameter Gas-Operated Piston Gages as Primary Pressure Standards

C.D. Ehrlich, R.G. Driver, P. Olvera (CENAM), P. Delajoud (DH Instruments), and M. Girard (DH Instruments)

Historically, mercury manometers have been used as primary laboratory standards to achieve the lowest estimated uncertainties of gas pressure measurements in the atmospheric pressure region. However, gas-operated deadweight piston gages have been the instrument of choice for most applications where high accuracy, low cost, ease of use, and transportability are important considerations in the transfer of the unit of pressure between laboratories or from the laboratory to the field. Recently, gas-operated deadweight piston gage technology has advanced to the point where it is becoming feasible to use these instruments as primary laboratory pressure standards, competitive with manometry. The Thermophysics Division is working to develop such primary gas-operated deadweight piston gages through independent research activities and through a Cooperative Research and Development Agreement (CRADA) with DH Instruments, Inc. and the NIST Dimensional Metrology Group (DMG).

To use a gas-operated deadweight piston gage as a primary standard, it is necessary to fabricate a piston and cylinder of suitable geometry and material, to make measurements of the geometry with acceptable levels of uncertainty, and to develop a physical/mathematical model of the instrument consistent with its laboratory behavior. A new type of gas-operated deadweight piston gage has been developed under the CRADA that has a piston/cylinder combination with a never-before-achieved nominal diameter of 50 mm. The piston and cylinder are made of a ceramic material that provides low thermal expansivity, light weight for lower-pressure operation (down to 2.5 kPa), and a good surface finish. The cylinder is the rotating element, and the gage is of a controlled-clearance design that operates in both the gage (atmospheric pressure above the piston) and absolute modes (essentially vacuum above the piston).

Thus far, three sets of pistons/cylinders have been fabricated, measured dimensionally, and tested for laboratory performance. Dimensional measurements showed these parts to be among the roundest ever seen by the NIST DMG; the nominal uncertainty in the dimensionally-measured effective areas of the gages is ±3 parts per million (ppm). In addition to this uncertainty, other factors related to the movement of the gas through the small annular region between the piston and the cylinder contribute to the overall uncertainty in the effective areas of the gages. These effects are being investigated experimentally via measurements of the ratios of the effective areas of the gages under various operating conditions (mode of operation and gas species). The measurements are being compared to theoretical models that take these effects into account, at least so far as the imperfections in the geometries of the gages are concerned. Preliminary results for nitrogen show the measured effective-area ratios to be consistent with the theoretical values at about the 2 ppm level, which is also the magnitude of the theoretical gage-to-absolute mode effective-area differences. Similar tests are in progress using helium as the operating gas. At the conclusion of the ratio measurements, the effective areas of the gages will be measured using instrumentation that traces to the NIST Gas Thermometer Manometer, to enable closure analyses of the absolute effective areas of the gages using two independent primary methods.

23. <u>Development of Vacuum and Leak Rate Standards for Sandia and the Navy</u>

S.A. Tison, P.J. Abbott, D.F. Martin, and F.G. Long

Many organizations require vacuum and leak rate measurement capabilities available only at national metrology laboratories such as NIST. Unfortunately, the number of calibrations required by these organizations often surpasses the resources of the national laboratory, or the frequency requires turn-around-times that could be accomplished only with on-site calibration. To address such needs, the Thermophysics Division has a tradition of developing state-of-the-art vacuum and leak rate calibration standards for other laboratories, most recently, Sandia National Laboratory and the Primary Standards Laboratory of the Department of the Navy.

For Sandia, a vacuum calibration system has been developed based upon a molecular orifice flow technique. This system generates known pressures over the range 10^{-4} to 10 Pa with corresponding uncertainties ranging from 2% to 1%. The system consists of a NIST-developed flow generator and two vacuum chambers separated by a restriction composed of one of three selectable, calibrated conductance elements. The flow from the flow generator passes through the upper chamber and conductance element into the lower chamber, which is connected to a vacuum pump. The pressure generated in the upper chamber (the target pressure) is determined by two quantities: the difference in pressure between the upper and lower chambers (determined by the known flow and known conductance of the flow restriction), and the ratio of the pressures in the upper and lower chambers (measured with a spinning rotor gage). This system is designed to calibrate low-range capacitance diaphragm gages, spinning rotor gages, and other vacuum instruments that operate in this pressure range. The system has been constructed and is currently being compared to existing primary standards at NIST; it will be delivered to Sandia in 1995.

For the Navy, a system has been developed to calibrate leaks over the range 10^{-14} to 10^{-6} mol/s with a variety of gases, including helium, nitrogen, argon, sulfur hexafluoride, and many refrigerants. The system uses four calibrated conductances with the appropriate pressure measuring instrumentation to generate known flows over its range of operation. These flows are compared with those of the leak artifacts to be calibrated. The system is totally automated and can calibrate leaks over the temperature range 0 to 100 °C and with variable reservoir fill pressures. The system has been completed during the past year and used by Navy personnel at NIST for calibration of their typical leak workload. After the completion of training of Navy personnel, the system will be delivered to the Navy.

24. Computational Studies of Transition-Range Flow Phenomena

J.P. Looney and R.D. Mountain

The understanding of a wide range of gaseous flow phenomena is important in the vacuum processing and equipment industries and in the development of primary vacuum and flow standards. However, while theories exist for the extremes of molecular and viscous flows, theories for flow in the transition regime are not as refined and their validity not as firmly established. Such flows are important in a wide variety of applications, including the modeling and control of gas fluxes in chemical vapor deposition and plasma processing, the design and operation of micro-machined gears and motors, and the design and operation of molecular-drag pumps and vacuum gages.

To better understand transition flow phenomena relevant to the development of primary vacuum standards, we have undertaken Monte-Carlo simulational studies during the past year of the flow of gas through an orifice in the near-molecular-flow regime where the mean free path in the gas is of the order or larger than the orifice diameter; for a 1-cm orifice and simple gases, this occurs for pressures below approximately 10 Pa. Our Monte-Carlo results for flows in this regime clearly elucidate the underlying physical mechanisms, including the relation between solutions derived from the Boltzmann equation and solutions obtained from intuitive mean-free-path arguments -- differences between these approaches arise from subtleties in the assumed gas-molecule-collision dynamics. The simulation results also are in good agreement with experimental data obtained using the Division's new Transition Range vacuum standard; thus, the simulations provide an extra degree of confidence in our understanding of the new standard.

25. Water: Its Measurement and Control in Vacuum Workshop

S.A. Tison, J.P. Looney, and C.R. Tilford

The measurement of contaminant gases in vacuum environments is important for the aerospace, semiconductor, and electronics industries, among others. Of particular importance is water vapor, which is a major contaminant in all of these industries and which has significant impacts on the performance, reliability, and usefulness of their products.

While the importance of water vapor as a contaminant is understood, its measurement and control is not. To facilitate discussion on this subject, a workshop on water measurement and control in vacuum environments was held at NIST on May 23-25, 1994. The objectives were to determine the present state of water vapor measurement and control technology in vacuum applications, to explore ways of industrial implementation, and to identify unsolved problems. The scope of the workshop included the assessment of the current understanding of the interaction of water with technical vacuum surfaces, the available techniques for modeling water outgassing from vacuum surfaces, cleaning techniques and surface treatments to minimize adsorbed water, water vapor measurement techniques in vacuum, and the identification of further research which would contribute to a better understanding of water in vacuum environments.

The three-day workshop consisted of 35 oral presentations followed by small group discussions on water-surface physics, surface modification and cleaning techniques, and water vapor measurement instrumentation. The approximately 80 attendees included participants from industrial, academic, and government institutions representing a number of different industries and disciplines, including the space, semiconductor, and electronic-components industries, as well as a number of manufacturers of vacuum equipment and instrumentation. The NIST Advanced Technology Program and the Vacuum Technology Division of the American Vacuum Society cosponsored the workshop with the Thermophysics Division.

The lectures and small group discussions identified a number of areas for which resources should be directed to solve problems associated with water vapor measurement and control. First, water adsorption isotherms on technical surfaces, such a stainless steel and aluminum, need to be measured with sufficient accuracy for validation of water transport models in vacuum environments. Second, removal of water vapor via chemical reaction with gas-phase reactants should be explored further to identify reactants which would produce products compatible with currently used vacuum materials. Third, design changes in traditional vacuum gages, such as quadrupole mass spectrometers, should be investigated to minimize deleterious effects such as sensitivity instabilities when used with active gases. Finally, optical water-vapor measurement techniques based on absorption and ionization offer much promise for sensitive and reliable water vapor measurement but should be refined so that instruments could become commercially available.

26. Quantitative Optical Measurements of UHV Pressures and Partial Pressures

J.P. Looney

In a wide variety of applications, the measurement and control of contaminant gases can be crucial to product yield, reliability, and process efficiency. However, the measurement of low number densities of gases in vacuum with conventional vacuum instrumentation is often limited, and the current generation of vacuum standards at NIST are restricted in their use to nitrogen and the rare gases. To address this situation, a program has been started to develop quantitative optical techniques to measure low densities of non-inert gases such as water, oxygen, and hydrogen in the ultra-high-vacuum (UHV) range.

During the past year, initial experiments on the use of resonance-enhanced multiphoton ionization (REMPI) of water near 248 nm showed good promise and indicated that the detection limit is near 10^{-8} Pa. However, the usefulness of REMPI to detect water in vacuum is hampered by a lack of detailed knowledge of the photoionization spectrum of water in two-photon absorption, three-photon ionization. Experiments are currently underway to survey the water three-photon ionization spectrum to identify strong features that could be used for quantitative measurements; to date, some five different bands have been investigated.

During the past year, we have also established collaborative efforts with the Process Measurements Division (836) and with Princeton University to determine the feasibility of using optical ring-down cavity (RDC) spectroscopy to measure low gas densities and concentrations, with a particular emphasis on water vapor. The RDC technique exploits recent advances in high reflectivity mirror technology in the form of optical cavities with extremely low optical losses. Within an RDC, photon energy densities decay (or "ring down") very slowly with time, and the photon decay time is a measure of the losses within the cavity. Under appropriate circumstances, the photon decay time is a direct measure of the density of the absorbing species in the cavity. To date, RDC spectroscopy has been utilized to detect and measure very weak absorptions in gases present in high concentrations. In contrast, our challenge is to detect strongly absorbing species present either at very low densities or at very low concentrations in mixtures. At present, a ring down cavity has been designed and constructed, and experiments have been initiated to establish more firmly the utility of this approach for quantitative measurements.

C. Outputs and Interactions (Thermophysics Division)

1. Publications

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2. Talks

Berg, R.F., "Science Overview of Critical Viscosity Experiment," NASA Lewis Research Center, Brook Park, OH, May 3, 1994.

Berg, R.F., "Hydrodynamic Similarity in an Oscillating Body Viscometer," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 22, 1994.

Bruno, T.J., "PCB Properties for Separation Processes," Gas Research Institute Meeting, Chicago, IL, October 21, 1993.

Bruno, T.J., "Alternative Refrigerants as Supercritical Fluid Solvents," 5th International Symposium on Supercritical Fluid Chromatography and Extraction, Baltimore, MD, January 11, 1994. Invited

Bruno, T.J., "Enthalpy of Adsorption for PCB Separation," Gas Research Institute Meeting, Chicago, IL, January 22, 1994.

Bruno, T.J., "Separation of PCB's from Natural Gas," International Forum on Process Analytical Chemistry," Conroe, TX, January 25, 1994.

Bruno, T.J., "Summary of Property Research for PCB Separation," Gas Research Institute Meeting, San Antonio, TX, January 27, 1994.

Bruno, T.J., "Applications of the Vortex Tube in the Laboratory," Colorado School of Mines, Golden, CO, April 18, 1994. Invited

Bruno, T.J., "Properties of Trace Contaminants in Natural Gas," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 20, 1994.

Butler, B.D., "Diffraction from Disordered Systems," CSTL-Boulder Seminar, NIST, Boulder, CO, September 6, 1994.

Defibaugh, D.R., "Compressed Liquid Densities, Saturated Liquid Densities and Vapor Pressures of 1,1,1,2,3,3 Hexafluoropropane (HFC-236ea)," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 21, 1994.

Doty, S.W., "Recent Developments in Gas Piston Gauge Research at NIST," Annual Meeting of the NCSL, Chicago, IL, August 3, 1994. Invited

Driver, R.G., "Recent Developments in Gas Piston Gauge Research at NIST," Annual Meeting of the NCSL, Chicago, IL, August 3, 1994. Invited

Ehrlich, C.D., "An Overview of International Pressure Metrology," 1994 Measurement Science Conference Symposium and Workshop, Pasadena, CA, January 27, 1994. Invited

Ehrlich, C.D., "High Pressure Metrology at NIST," National Institute of Metrology, Beijing, People's Republic of China, March 10, 1994. Invited

Ehrlich, C.D., "Pressure Metrology at NIST," National Institute of Metrology, Beijing, People's Republic of China, March 11, 1994.

Ehrlich, C.D., "The NIST NVLAP Program," National Laboratory of Metrology, Tsukuba, Japan, March 17, 1994.

Ehrlich, C.D., "Status of the Deadweight Pressure Gage RISP," National Conference of Standards Laboratories, Chicago, IL, August 3, 1994. Invited

Ehrlich, C.D., "A Look at Uncertainties Over Twenty Decades of Pressure Measurement," XIII IMEKO World Congress, Turin, Italy, September 7, 1994. Invited

Filippelli, A.R., "Some Measurements of Sensitivity, Linearity, and Stability in Several Commercial Extractor Gauges," 40th National Symposium of the American Vacuum Society, Orlando, FL, November 18, 1993.

Friend, D.G., "Modeling the Properties of Air at Very High Temperatures and Pressures," Hypersonic Wind Tunnel Workshop, Princeton, NJ, December 6, 1993. Invited

Friend, D.G., "Standard Reference Databases for the Thermophysical Properties of Fluids," American Chemical Society National Meeting, San Diego, CA, March 13, 1994.

Friend, D.G., "Computerized Databases and Modeling Activities for the Thermophysical Properties of Fluids," Union Carbide, Charleston, WV, May 18, 1994.

Friend, D.G., "Computerized Databases and Modeling Activities for the Thermophysical Properties of Fluids," Dow Chemical, Midland, MI, May 19, 1994.

Friend, D.G., "Computerized Databases and Modeling Activities for the Thermophysical Properties of Fluids," Michigan Technological University, Houghton, MI, May 20, 1994.

Friend, D.G. and Huber, M.L., "Calculation of Melting Lines Using a Density Functional Theory," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 22, 1994.

Friend, D.G., "Standard Thermophysical Properties of the Ammonia-Water Binary Fluid," 12th International Conference on the Properties of Water and Steam, Orlando, FL, September 15, 1994.

Gillis, K.A., "An Acoustic Viscometer for Measurements in Gases," 127th Meeting of the Acoustical Society of America, Cambridge, MA, June 6, 1994.

Gillis, K.A., "An All-Metal Collection System for Preparation of Ultra-High Purity Low Boiling Compounds," International Symposium on Preparative Chromatography, Washington, DC, June 12, 1994.

Gillis, K.A., "Acoustic Methods for Absolute Thermal Conductivity Measurements in Gases," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 23, 1994.

Gillis, K.A., "Thermodynamic Properties of Several Halogenated Hydrocarbons from Acoustic Measurements," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 23, 1994.

Gillis, K.A., "Acoustic Methods for Transport Property Measurements in Gases," Physical Acoustics Summer School, Pacific Grove, CA, June 27, 1994.

Hanley, H.J.M., "A SANS Study of Gelation," Imperial College, London, United Kingdom, February 10, 1994.

Hanley, H.J.M., "A Sans Study of Gelation," Technical University of Berlin, Berlin, Germany, April 5, 1994. Invited

Hanley, H.J.M., "Fluids, Who Cares?", Boulder Laboratories Colloquium, NIST, Boulder, CO, May 2, 1994.

Hanley, H.J.M., "Research on Liquids in the Twentieth Century," Chemical Science and Technology Laboratory Colloquium, NIST, Gaithersburg, MD, June 8, 1994. Invited

Hansen, B.N., "Advantages of Supercritical Fluid Extraction and Supercritical Fluid Chromatography," University of Colorado, Boulder, CO, March 17, 1994. Invited

Hansen, B.N. and Bruno, T.J., "Solubility of Natural Products in Supercritical Fluid Alternative Refrigerant Solvents," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, Colorado, June 21, 1994.

Haynes, W.M., "Densities of Natural Gas Liquids," Gas Processors Association 73rd Annual Convention, New Orleans, LA, March 7, 1994. Invited

Haynes, W.M., "Experimental Program at NIST for the Thermophysical Properties of Fluids," Union Carbide, Charleston, WV, May 18, 1994.

Haynes, W.M., "Experimental Program at NIST for the Thermophysical Properties of Fluids," Dow Chemical, Midland, MI, May 19, 1994.

Haynes, W.M., "Experimental Program at NIST for the Thermophysical Properties of Fluids," Michigan Technological University, Houghton, MI, May 20, 1994.

Holcomb, C.D., "Evaluation of Reference Fluid Selection for Corresponding States Theories and Correlations for Coexisting Densities, Vapor Pressures, and Surface Tensions," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 22, 1994.

Holcomb, C.D. and Rainwater, J.C., "Evaluation of High Pressure Thermodynamic Consistency Test Using Ethane + Propane and Propane + n-Butane Data in the Critical Region," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 24, 1994.

Holste, J.C., Jaeschke, M., Schouten, J., and Haynes, W.M., "Standard Reference Density Data for Natural Gas Mixtures," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 20, 1994. Invited

Huber, M.L. and Friend, D.G., "Thermophysical Property Standard Reference Data from NIST," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 22, 1994.

Kayser, R.F., "Research on Physical and Chemical Properties at NIST," Union Carbide Corporation, Charleston, WV, May 18, 1994.

Kayser, R.F., "Research on Physical and Chemical Properties at NIST," Dow Chemical Company, Midland, MI, May 19, 1994.

Kayser, R.F., "Research on Physical and Chemical Properties at NIST," Michigan Technological University, Houghton, MI, May 20, 1994.

Kayser, R.F. and Haynes, W.M., "Research on Physical and Chemical Properties at NIST," Workshop on Fluid Processes and Properties Utilized in Process Design and Simulation, NIST, Boulder, CO, August 23, 1994.

Kayser, R.F. and McLinden, M.O., "Thermophysical Properties of Alternative Refrigerants," DOE Office of Building Technologies Program Review, Gaithersburg, MD, September 16, 1994.

Laesecke, A.R., "Global Change: A Chance for Regenerative Thermal Machines?", Boulder Renewable Energy Association, Boulder, CO, October 26, 1993. Invited

Laesecke, A.R., "Viscosity Measurements and Correlation of Liquid 2,2,2-Trifluoroethanol (TFE) + E181 Mixtures," IUPAC Subcommittee on Transport Properties Meeting, Boulder, CO, June 18, 1994.

Laesecke, A.R. and Perkins, R.A., "Observations of Polar Fluid Behavior in Hot-Wire Thermal Conductivity Instruments," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 22, 1994.

Looney, J.P., "Measurements of CO Pressures in the UHV Regime Using Resonance-Enhanced Multiphoton Ionization Time-of-Flight Mass Spectroscopy," 40th National Symposium of the American Vacuum Society, Orlando, FL, November 17, 1993. Invited

Looney, J.P., "Laser Ionization Measurements of Gas Pressures in Vacuum: Present Status and Future Possibilities," International Workshop on Extreme High Vacuum (XHV'94), Tsukuba, Japan, April 21, 1994. Invited

Looney, J.P., "Measurement of Gas Densities in the UHV-Regime Using Laser Photoionization," Korean Research Institute of Standards and Science (KRISS), Taejon, Korea, April 25, 1994. Invited

Looney, J.P., "Measurements of Gas Densities in the UHV Regime Using Laser Photoionization," Korean Atomic Energy Research Institute, Daejon, Korea, April 25, 1994. Invited

Looney, J.P., "Measurements of Gas Densities in the UHV Regime Using Laser Photoionization," Seoul National University, Seoul, Korea, April 27, 1994. Invited

Looney, J.P., "Measurement of Water Vapor Densities in the UHV Using Laser Photoionization," Workshop on Water: Its Measurement and Control in Vacuum, NIST, Gaithersburg, MD, May 24, 1994.

Louie, B., "Mechanism of Gas Permeation Through Microporous Ceramic Membranes at Cryogenic Temperatures," University of Oxford, Oxford, United Kingdom, December 8, 1993.

Louie, B., "Gas Permeation Through Porous Ceramic Membranes at Cryogenic Temperatures," 1994 North American Membrane Society Meeting, Breckenridge, CO, May 23, 1994.

MacDonald, R.A., "Analytical Method for Determining Thermal Conductivity from Dynamic Experiments: Application to Tungsten," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 21, 1994.

MacDonald, R.A., "Vapor-Liquid Equilibrium of New Refrigerant Mixtures: HFC32/HFC134a and HCFC123/HFC134a," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 24, 1994.

Magee, J.W., "Isochoric (p,ρ,T) Measurements on Difluoromethane (R32) and Pentafluoroethane (R125) from Their Triple-Point Temperature to 400 K at Pressures to 35 MPa," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 21, 1994.

McLinden, M.O., "Thermophysical Properties of Alternative Refrigerants - Status of the HFCs," ASME Winter Annual Meeting, New Orleans, LA, December 3, 1994. Invited

McLinden, M.O., "Replacing the CFCs: The Possibilities, Realities, and Status of Thermophysical Properties in an Uncertain Environment," Japanese Association of Refrigeration International Seminar on Heat Transfer, Thermophysical Properties, and Cycle Performance of Alternative Refrigerants, Kitakyshu, Japan, December 7, 1993. Invited

McLinden, M.O., "Measurement of the PVT Properties and Formulation of an Equation of State for Refrigerant 124 (1-chloro-1,2,2,-tetrafluoroethane)," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 21, 1994.

McLinden, M.O., "Thermophysical Properties of Alternative Refrigerants: Status, Needs, and Future Possibilities," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 21, 1994. Invited

Miiller, A.P., "A Study of Low-Pressure Measurement Performance of Capacitance Diaphragm Gages," 40th National Symposium of the American Vacuum Society, Orlando, FL, November 18, 1993.

Miiller, A.P., "Development of Improved Low-Pressure Measurement Transfer Standards", 17th NASA Metrology and Calibration Workshop, NIST, Boulder, CO, April 28, 1994.

Mountain, R.D., "Supercooled Liquids and Glasses: MD Simulations," 2nd IMACS International Conference on Computational Physics, St. Louis, MO, October 6, 1993.

Mountain, R.D., "Molecular Dynamics Simulation of Nonequilibrium Processes - A Cautionary Tale," Process Measurements Division Seminar, NIST, Gaithersburg, MD, November 18, 1993.

Mountain, R.D., "Simulation Studies of Supercooled and Glass Forming Liquids," Department of Physics, The Catholic University of America, Washington, DC, December 16, 1993.

Mountain, R.D., "Simulation Studies of Supercooled and Glass Forming Liquids," XXIII Winter Meeting on Statistical Physics, Cuernavaca, Mexico, January 11, 1994.

Narayan, A.P., Rainwater, J.C., and Hanley, H.J.M., "Non-Newtonian Flow Between Concentric Cylinders Using Thermophysical Properties Obtained from Simulations," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 22, 1994.

Outcalt, S.L. and McLinden, M.O., "Equations of State for the Thermodynamic Properties of R32 (Difluoromethane) and R125 (Pentafluoroethane)," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 21, 1994.

Pellegrino, J.J., "Chitin: Old/New Material for Membranes," 11th Annual Membrane Technology/Separations Planning Conference, Newton, MA, October 12, 1993.

Pellegrino, J.J., "Low Temperature H_2S Separation Using Membrane Reactor with Redox Catalyst," Fuels Technology Contractors Review Meeting, Morgantown, WV, November 18, 1993.

Pellegrino, J.J., "CO_2/CH_4 Transport in Polyperfluorosulfonate Ionomers: Effects of Polar Solvents on Permeation and Solubility," 1994 North American Membrane Society Meeting, Breckenridge, CO, May 23, 1994.

Pellegrino, J.J., "Polyaniline Gas Separations: Sorption Measurements and Mechanistic Insights," Gordon Research Conference on Separation and Purification, New London, NH, August 4, 1994. Invited

Pellegrino, J.J., "Polyaniline Gas Separation Polymer: Sorption Measurements and Mechanisms," CSTL-Boulder Colloquium, NIST, Boulder, CO, August 12, 1994.

Perkins, R.A., "Measurements of Alternative Refrigerant Thermal Conductivity," 22nd International Thermal Conductivity Conference, Tempe, AZ, November 8, 1993.

Perkins, R.A., "Measurement of Thermal Properties of Electrically Conducting Fluids Using Transient Hot Wires," 12th Symposium on Energy Engineering Sciences, Argonne National Laboratory, Argonne, IL, April 27, 1994.

Perkins, R.A., "Summary of NIST Thermal Conductivity Measurements on the R134a Round Robin Sample," IUPAC Subcommittee on Transport Properties Meeting, Boulder, CO, June 18, 1994.

Perkins, R.A., "Thermal Conductivity of R152a," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 22, 1994.

Perkins, R.A. and Laesecke, A.R., "Thermal Radiation Corrections in Transient Hot Wire Measurements of Thermal Conductivity," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 22, 1994.

Peskin, A.P. and Hardin, G.R., "Overview of Object-Oriented Programming," CSTL-Boulder Seminar, NIST, Boulder, CO, September 28, 1994.

Rainwater, J.C., "A Nonlinear Correlation of High-Pressure Vapor-Liquid Equilibrium Data for Ethylene and n-Butane Showing Inconsistencies in Experimental Compositions," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 20, 1994.

Rainwater, J.C., "A Nonclassical Model of a Type 2 Mixture with Vapor-Liquid and Liquid-Liquid Equilibria Connected by a Three-Phase Locus," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 23, 1994.

Rainwater, J.C., "Quantum Collisional Transfer Contributions to the Density Dependence of Gaseous Viscosity," 19th International Symposium on Rarefied Gas Dynamics, Oxford, United Kingdom, July 25, 1994.

Rainwater, J.C., "Phase Equilibria of Mixtures in the Critical Region," Dept. of Chemical Engineering, University of South Florida, Tampa, Florida, September 9, 1994. Invited

Rainwater, J.C., "An Asymptotic Expression for Phase Boundaries of Mixtures with a Dilute Nonvolatile Solute: Application to Aqueous Salt Systems," 12th International Conference on the Properties of Water and Steam, Orlando, FL, September 14, 1994.

Schmidt, J.W., "Alternative Refrigerants R245fa and R143a: Critical Temperature, Refractive Index, Surface Tension and Estimates of Liquid, Vapor and Critical Densities," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 23, 1994.

Sengers, J.M.H. Levelt, "Application of the Taylor Dispersion Method in Supercritical Fluids," American Institute of Chemical Engineers Annual Meeting, St. Louis, MO, November 8, 1993.

Sengers, J.M.H. Levelt, "Supercritical Water Oxidation for Hazardous Waste Destruction," North Carolina State University, Raleigh, NC, February 1994. Invited

Sengers, J.M.H. Levelt, "Supercritical Fluids, Properties and Applications," University of Wisconsin-Madison, Madison, WI, March 24, 1994. Invited

Sengers, J.M.H. Levelt, "Significant Contributions of IAPWS to the Power Industry, Science and Technology," 12th International Conference on the Properties of Water and Steam, Orlando, FL, September 12, 1994. Invited

Sengers, J.V., "Fluctuations in Liquids in Non-Equilibrium Steady States," Physics Department, The Catholic University of American, Washington, DC, January 27, 1994. Invited

Sengers, J.V., "Fluctuations in Fluid Systems in Stationary Non-Equilibrium States," Gordon Conference on Polymer Physics, Newport, RI, August 1, 1994. Invited

Tilford, C.R., Browning, D.F., and Looney, J.P., "A PC-Based Spinning Rotor Gage Controller," 40th National Symposium of the American Vacuum Society, Orlando, FL, November 18, 1993.

Tilford, C.R., "The Measurement of XHV-Range Partial Pressures," International Workshop on Extreme High Vacuum (XHV'94), Tsukuba, Japan, April 20, 1994. Invited

Tilford, C.R., "Process Monitoring with RGAs: Limiting Factors," International Conference on Metallurgical Coatings and Thin Films, San Diego, CA, April 27, 1994.

Tilford, C.R., "The Effects of Water Vapor on Vacuum Instruments," Water: Its Measurement and Control in Vacuum Workshop, NIST, Gaithersburg, MD, May 24, 1994.

Tison, S.A., "Transition Flow in Vacuum Metrology," Physikalisch-Technische Bundesanstalt (PTB) Colloquium, Berlin, Germany, October 1, 1993. Invited

Tison, S.A., "Vacuum Metrology at NIST," 1993 National Conference of the Indian Vacuum Society, National Physical Laboratory (NPL), New Delhi, India, October 7, 1993. Invited

Tison, S.A., "Slip and Transition Flow in Vacuum Systems," 1993 National Conference of the Indian Vacuum Society, National Physical Laboratory (NPL), New Delhi, India, October 8, 1993. Invited

Tison, S.A., "Utilizing Quadrupole Gas Analyzers for Industrial Leak Testing," American Society for Nondestructive Testing (ASNT) 1993 Fall Conference, Long Beach, CA, November 10, 1993. Invited

Tison, S.A., "Characteristics of Polymer Membranes Used to Generate Known Gas Flows," 40th National Symposium of the American Vacuum Society, Orlando, FL, November 17, 1993.

Tison, S.A., "Low-Flow Calibration System," 40th International Instrumentation Symposium, Baltimore, MD, May 5, 1994.

Tison, S.A., "Pressure and Vacuum Metrology and Industrial Development," U.S. Mission to the Organization of American States, Buenos Aires, Argentina, May 30, 1994.

Tison, S.A., "Pressure Measurements, Standards, and Calibrations," U.S. Mission to the Organization of American States, Buenos Aires, Argentina, June 1, 1994.

Tison, S.A., "Pressure and Vacuum Metrology and Industrial Development," U.S. Mission to the Organization of American States, San Jose, Costa Rica, August 16, 1994. Invited

Tison, S.A., "Pressure Measurements, Standards, and Calibrations," U.S. Mission to the Organization of American States, San Jose, Costa Rica, August 17, 1994. Invited

Tison, S.A., "Leak Testing Fundamentals," ASNT 1994 Fall Conference, Atlanta, GA, September 23, 1994. Invited

Van Poolen, L.J. and Rainwater, J.C., "Vapor-Liquid Equilibria of Ternary Mixtures in the Critical Region on Paths of Constant Temperature and Overall Composition," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 23, 1994.

Watts, L.A., "The Solubility of ZnO in Supercritical H_2O-$NaC\ell$," CSTL-Boulder Colloquium, NIST, Boulder, CO, April 22, 1994.

Weber, L.A., "Ebulliometers for Measuring the Thermodynamic Properties of Fluids and Fluid Mixtures," 12th Symposium on Energy Engineering Sciences, Argonne National Laboratory, Argonne, IL, April 27, 1994.

Weber, L.A. "Ebulliometers for Measuring the Thermodynamic Properties of Fluids and Fluid Mixtures," Thermophysics Division Seminar, NIST, Boulder, CO, May 4, 1994.

Weber, L.A., "A Model for Calculating Virial Coefficients of Natural Gas Hydrocarbons with Impurities," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 24, 1994.

Weber, L.A., "The Virial Coefficients of Five Binary Mixtures of Fluorinated Methanes and Ethanes," 12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, June 24, 1994.

Weber, L.A., "Report on the Design and Testing of a New High Pressure Ebulliometer for Studying the Thermodynamics of Refrigerant Mixtures," Fifth International Refrigeration Conference, Purdue University, West Lafayette, IN, July 19, 1994.

3. Cooperative Research and Development Agreements (CRADAs) and Consortia

Development of a Primary Pressure Standard for Gauge and Absolute Pressure Using Different Gases in the Range 2.5 to 175 kPa, C.D. Ehrlich
DH Instruments, Inc. (CRADA)

Micelle/Inorganic Complexes, H.J.M. Hanley
Exxon Research and Engineering Company (CRADA)

4. Patent Awards and Applications

Bruno, T.J., "Sample Cell for Infrared Spectrophotometry," Patent No. 5,280,177 (issued January 18, 1994)

Hansen, B.N., "Methods and Apparatus for Drug Delivery Using Supercritical Solutions," (filed August 1994)

Moldover, M.R., "Acoustic Cavities for Measuring Thermal Diffusivity and Viscous Diffusivity of Gases," (filed April 1994)

Pellegrino, J.J., Ko, M.Y., and Marko, P., "Methods of Making and Using Improved Microporous Hollow Fibers, the Improved Hollow Fibers and Tube Bundles Constructed of the Improved Fibers," Patent No. 5,258,202 (issued November 2, 1993)

5. SRM Activities

None

6. SRD Activities

SRD 4	NIST Thermophysical Properties of Hydrocarbon Mixtures Database, Upgrade in Progress
SRD 10	NIST Thermophysical Properties of Water Database, Support
SRD 12	NIST Thermophysical Properties of Pure Fluids Database, Upgrade in Progress
SRD 14	NIST Mixture Properties Program Database, Upgrade in Progress
SRD 23	NIST Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Database (REFPROP), Upgrade Release, Support

7. Calibrations

Calibration services (pressure, vacuum, and leak rate) have been provided for the following organizations:

Allied Signal Aerospace
Ametek Inc.
Babcock & Wilcox
Boeing Defense & Space Group
Center for Measurement Standards
Consumers Power Co.
Duke Power Co.
Eastman Kodak Co.
EG&G Rocky Flats, Inc.
General Dynamics
General Electric Aircraft
Granville-Phillips Co.
GTE California
Helium Leak Testing, Inc.
LDS Vacuum Products, Inc.
Leybold Inficon

Lockheed Missiles & Space Co.
Martin Marietta Corp.
Martin Marietta Energy Systems
MKS Instruments Inc.
NASA Kennedy Space Center
Naval Warfare Assessment Center
Newark Air Force Base
NSI Technology Services Corp.
PECO Energy Co.
Pressurements LTD
Rockwell International
Ruska Instrument Corp.
Sandia National Laboratory
TRW Space & Defense Sector
TRW Equipment Management Center
U.S. Army Test Meas. & Diagnostic Equip. Activity
Vacuum Instrument Corp.
Varian
VEECO Instruments Inc.
Willson Scientific Glass Inc.

8. Committee Assignments

T.J. Bruno

- International Forum on Process Analytical Chemistry, Scientific Board
- ASTM Committee D03 on Gaseous Fuels
- Gas Research Institute PCB Task Force
- Annual SFE-SFC International Symposium, Technical Board

C. Ehrlich

- BIPM Consultative Committee for Mass and Related Quantities, Working Groups on High Pressure and Medium Pressure
- ASTM Committee E07 on Nondestructive Testing
- ASTM Subcommittee E07.08 on Leak Testing
- AVS Calibrated Leak Subcommittee (Co-Chair)
- NCSL Recommended Practices Committee on Deadweight Standards (Chair)

A.R. Filippelli

- AVS Recommended Practices Committee on the Calibration of Mass Spectrometers for Partial Pressure Analysis

D.G. Friend

International Association for the Properties of Water and Steam, Working Group on Thermophysical Properties of Water and Steam

ASME, Research Subcommittee on the Properties of Water and Steam

J.S. Gallagher

ASME Research and Technology Committee on Water in Thermal Power Systems

ASME Research Subcommittee on the Properties of Water and Steam (Secretary)

International Association for Properties of Water and Steam, Working Group on Thermophysical Properties of Water and Steam

IAPWS Task Group for the Evaluation of New Scientific Formulations for Water and Steam (Chair)

H.J.M. Hanley

ASME K-7 Thermophysical Properties Committee

Subcommittee on Transport Properties of IUPAC Commission I.2: Thermodynamics

W.M. Haynes

International Energy Agency Annex 18 - Thermophysical Properties of Environmentally Acceptable Refrigerants

ASTM Committee D03 on Gaseous Fuels

ASTM Subcommittee D03.08 on Thermophysical Properties of Gaseous Fuels (Chair)

ASME K-7 Thermophysical Properties Committee

12th Symposium on Thermophysical Properties, Local Organizing Committee

13th Symposium on Thermophysical Properties, Program Committee (Chair)

R.W. Hyland

AVS Recommended Practices Committee on the Use of Capacitance Diaphragm Gages

R.F. Kayser

AIChE Design Institute for Physical Properties Research (DIPPR), NIST Technical Representative

Steering Committee Member, DIPPR Project 801: Data Compilation; 805: Experimental Data on Mixtures; 851: Critical Properties of Pure Compounds; 871: Pure Component Ideal Gas Enthalpies of Formation; 882: Evaluated Data of Mixtures; 911: Environmental, Safety, and Health Data Compilation; and 931: Data Prediction Methods

A.R. Laesecke

Subcommittee on Transport Properties of IUPAC Commission I.2: Thermodynamics

IUPAC Subcommittee on Transport Properties Meeting, Local Organizing Committee

B. Louie

University of Colorado Chemical Engineering Advisory Committee

M.O. McLinden

ASHRAE Technical Committee 3.1 - Refrigerants and Brines
International Energy Agency Annex 18 - Thermophysical Properties of Environmentally Acceptable Refrigerants (Operating Agent/Chair)

A.P. Miiller

ASTM Committee E37 on Thermal Measurements

M.R. Moldover

NASA Proposal Review Panel on Metals and Alloys Containerless Processing
NASA Review Panel, Fluid Dynamics Discipline Working Group
NASA Review Panel, Fundamental Processes Discipline Working Group

J.J. Pellegrino

Interagency Consortium on Desalination and Membrane Separations Research
AIChE Separations Division - Electronic Bulletin Board Coordinator

R.A. Perkins

ASTM Committee D34 on Waste Management
Subcommittee on Transport Properties of IUPAC Commission I.2: Thermodynamics
IUPAC Subcommittee on Transport Properties, Local Organizing Committee

J.M.H. Levelt Sengers

International Association for Properties of Water and Steam (U.S. National Delegate)
International Association for Properties of Water and Steam, Working Group on Thermophysical Properties of Water and Steam
International Association for Properties of Water and Steam, Working Group on Physical Chemistry of Aqueous Systems
12th Symposium on Thermophysical Properties, Program Committee (Chair)
Advisory Committee of the Chemistry Division, Oak Ridge National Laboratory
Bueche and Founders Awards Committee, National Academy of Engineering

J.V. Sengers

ASME K-7 Thermophysical Properties Committee
ASME Research and Technology Committee on Water and Steam in Thermal Power Systems
ASME Heat Transfer Division, Touloukian Award Subcommittee
International Association for Properties of Water and Steam, Working Group on Thermophysical Properties of Water and Steam
12th International Conference on the Properties of Water and Steam, Program Committee (Co-Chair)
Subcommittee on Transport Properties of IUPAC Commission I.2: Thermodynamics

C.R. Tilford

BIPM Consultative Committee for Mass and Related Quantities, Working Groups on Medium and Low Pressure (Chair)

S.A. Tison

ASTM Subcommittee E07.08 on Leak Testing (Vice Chair)

L.A. Weber

ASTM Committee E37 on Thermal Measurements

9. Editorships

T.J. Bruno

CRC Handbook of Alternative Refrigerant Analysis (Editor)

H.J.M. Hanley

International Journal of Thermophysics (Editorial Board)

W.M. Haynes

Journal of Chemical & Engineering Data (Editorial Board)

R.F. Kayser

IUPAC Volume on the Equations of State for Fluids and Fluid Mixtures (Editorial Board)

J.J. Pellegrino

Gas Separation and Purification (Editorial Board)

J.M.H. Levelt Sengers

Journal of Supercritical Fluids (Editorial Board)
"Supercritical Fluids; Fundamentals for Application," NATO Advanced Science Institute Series E, Vol. 273, Kluwer Academic Publishers, Dordrecht, Netherlands (1994) (Co-Editor)
Proceedings of the 12th Symposium on Thermophysical Properties, International Journal of Thermophysics (Co-Editor)

J.V. Sengers

International Journal of Thermophysics (Associate Editor)
Physica A (Editorial Board)
Journal of Non-Equilibrium Thermodynamics (U.S. Editor)
IUPAC Volume on the Equations of State for Fluids and Fluid Mixtures (Editorial Board, Chair)
Proceedings of the 12th International Conference on the Properties of Water and Steam (Editorial Committee, Chair)

C.R. Tilford

Vacuum (Editorial Board)

10. Seminars (Outside Speakers)

October 8, 1993

David R. Rector, Pacific Northwest Laboratories, Richland, WA, "Molecular Simulation of Fluid Phase Coexistence." (Division Sponsor: D.G. Friend)

January 18, 1994

Greg Swift, Los Alamos National Laboratory, Los Alamos, NM, "Thermoacoustic Engines." (Division Sponsor: M.R. Moldover)

March 3, 1994

Anders Wallqvist, Frederick Cancer Research and Development Center, Frederick, MD, "Hydrophobic Interactions." (Division Sponsor: R.D. Mountain)

May 11, 1994

S. Fred Singer, Department of Environmental Sciences, University of Virginia, Arlington, VA, "Stratospheric Ozone: Politically Correct and Other Views." (Division Sponsor: T.J. Bruno)

May 16, 1994

Bharat Soni, NSF Engineering Research Center for Computational Field Simulation, Mississippi State University, Mississippi State, MS, "Computational Field Simulation for Complex Physics/Complex Geometry." (Division Sponsors: A.P. Peskin and G.R. Hardin)

May 20, 1994

Yong Soo Kang, Korean Institute of Science and Technology, Seoul, Korea "Analysis of Facilitated Transport in Polymeric Membranes with Fixed-Site Carrier: Single RC Circuit Model." (Division Sponsor: J.J. Pellegrino)

June 10, 1994

Michael Caciari, Fort Lupton High School, Fort Lupton, CO, "Standard GC Retention Parameters for the Identification of Alternative Refrigerant Products." (Division Sponsor: T.J. Bruno)

June 13, 1994

William Klein, Boston University, Boston, MA, "Structure and the Breakdown of the Linear Cahn-Hilliard-Cook Theory." (Division Sponsor: R.D. Mountain)

August 5, 1994

Sandy A. Klein, Department of Mechanical Engineering, University of Wisconsin - Madison, Madison, WI, "Development and Use of Energy Analysis Software." (Division Sponsor: M.O. McLinden)

August 15, 1994

Allan H. Harvey, Simulation Sciences, Brea, CA, "The Role of Thermophysical Properties in Process Simulation." (Division Sponsor: W.M. Haynes)

August 17, 1994

Eric W. Lemmon, Center for Applied Thermodynamic Studies, University of Idaho, Moscow, ID, "Current Research at the Center for Applied Thermodynamic Studies (CATS) at the University of Idaho." (Division Sponsor: W.M. Haynes)

August 19, 1994

Lambert J. Van Poolen, Department of Engineering, Calvin College, Grand Rapids, MI, "Critical Pressure, Density, and Composition of Binary Mixtures Based on Isothermal Liquid-Vapor Data Application: CO_2-C_3H_8, CO_2-nC_4H_{10}, C_2H_6-C_3H_8, C_3H_8-nC_4H_{10}." (Division Sponsor: W.M. Haynes)

August 30, 1994

Jorge Orozco-Velazco, Institute of Physics, National University of Mexico, Mexico, "Transport Properties of Dense Fluids Using the Effective Diameter Hard Sphere Theory (EDHST): Review." (Division Sponsors: D.G. Friend and J.C. Rainwater)

September 22, 1994

Sergei B. Kiselev, Russian Academy of Science, Moscow, Russia, "Metastable States and Nucleation in Water." (Division Sponsor: J.M.H. Levelt Sengers)

September 26, 1994

Rakesh Malhotra, University of Tennessee, Knoxville, TN, "Tait Equation: Correlation and Prediction of Volumetric Properties of Fluids." (Division Sponsor: L.A. Weber)

September 26, 1994

Paulette Clancy, Cornell University, Ithaca, NY, "Comparison of Two Approaches to Simulating Crystal Growth at the Atomic Level." (Division Sponsor: R.D. Mountain)

11. Conferences/Workshops/Sessions Sponsored/Co-Sponsored

October 31 - November 2, 1993

National Water Research Institute, NSF Workshop on Fouling and Module Design, Newark, DE (J.J. Pellegrino)

November 7-12, 1993

AIChE Annual Meeting, St. Louis, MO
Co-organized sessions on Experimental and Theoretical Studies of Transport Properties (J.M.H. Levelt Sengers)

November 30, 1993

NIST/ATP Workshop on Supercritical Fluid Extraction: Technology of the Future, NIST, Boulder, CO (T.J. Bruno)

March 28-30, 1994

Precision Measurement Workshop on Vacuum Calibrations, NIST, Gaithersburg, MD (R. Hyland)

April 20-22, 1994

Precision Measurement Workshop on the Calibration and Use of Piston Gauges, NIST, Gaithersburg, MD (C.D. Ehrlich)

May 23-25, 1994

NIST/AVS/ATP Workshop on Water: Its Measurement and Control in Vacuum, NIST, Gaithersburg, MD (J.P. Looney and S.A. Tison)

June 19-24, 1994

12th Symposium on Thermophysical Properties, University of Colorado, Boulder, CO, Co-organized and chaired conference (J.M.H. Levelt Sengers), organized twelve sessions and one panel discussion on Refrigerants (M.O. McLinden), three sessions on Low Gravity (R.F. Berg), seven sessions on Natural Gas (W.M. Haynes), five sessions on Molecular Simulations (R.D. Mountain), four sessions on Supercritical Fluids (T.J. Bruno, J.M.H. Levelt Sengers), two sessions on Databases (M.L. Huber, D.G. Friend), two sessions on Data Correlation (D.G. Friend, M.L. Huber), four sessions on Database Demonstrations (M.L. Huber, D.G. Friend), four sessions on Shear Effects (J.V. Sengers), two sessions on Acoustics (M.R. Moldover), and three sessions on Structure of Fluids (H.J.M. Hanley)

July 19-20, 1994

NIST Workshop on Environmental Separations, NIST, Boulder, CO (T.J. Bruno and A.P. Peskin)

September 11-16, 1994

12th International Conference on the Properties of Water and Steam, Orlando, FL
Co-organized four sessions on Hydrothermal Oxidation (J.M.H. Levelt Sengers) and three sessions on Computer Simulations (R.D. Mountain)

VIII. Glossary

RSA	Republic of South Africa

Federal Agencies and Departments

ADAMHA	Alcohol, Drug Abuse, and Mental Health Administration
AFB	Air Force Base
AFTAC	Air Force Technical Applications Center
AMMTAP	Alaska Marine Mammal Tissue Archival Project
ATP	Advanced Technology Program
BRFL	Building Fire Research Laboratory
CAML	Computing and Applied Mathematics Laboratory
CCG	Calibration Coordination Group of the Department of Defense
CRDEC	Chemical Research, Development & Engineering Center
DMG	NIST Dimensional Metrology Group
DoD	Department of Defense
DoE	Department of Energy
EEEL	Electronics and Electrical Engineering Laboratory
EPA	Environmental Protection Agency
ERDEC	U.S. Army Edgewood Research and Development Engineering Command
FBI	Federal Bureau of Investigations
FDA	Food and Drug Administration
IAEA	International Atomic Energy Agency
LANL	Los Alamos National Laboratory
MEL	Manufacturing Engineering Laboratory
MSEL	Materials Science and Engineering Laboratory
NASA	National Aeronautics and Space Administration
NBS	National Bureau of Standards
NCI	National Cancer Institute
NIDA	National Institute on Drug Abuse
NIDDK	National Institute of Diabetes, Digestive and Kidney Diseases
NIDR	National Institute for Dental Research
NIH	National Institutes of Health
NIST	National Institute of Standards and Technology
NMI	Measurement Institute of the Netherlands
NMMTB	National Marine Mammal Tissue Bank
NOAA	National Oceanic and Atmospheric Administration
NREL	National Renewable Energy Laboratory
NRL	Naval Research Laboratory
NSF	National Science Foundation
OARD	Organic Analytical Research Division
RTI	Research Triangle Institute
SRDP	Standard Reference Data Program
SRM	Standard Reference Materials
USEPA	United States Environmental Protection Agency

WHOI	Woods Hole Oceanographic Institute
WRDC	Wright Research and Development Center

Foreign Standards Laboratory

BIPM	International Bureau of Weights and Measures (Paris)
CENAM	Centro Nacional de Metrologia (Mexico)
CCT	Comite Consultatif de Thermometrie
CIPM	International Committee of Weights and Measures
IAEA	Internatonal Atomic Energy Agency
IEC	International Electrotechnical Commission
IMEKO	International Measurement Congress
IMGC	Instituto di Metrologia "G. Colennetti" (Italy)
INSA de Rouen	l'Institut Nationale Scientifique Appliquee (Rouen France)
IPMI	International Precious Metals Institute
IUPAC	International Union of Pure and Applied Chemistry
KRISS	Korean Research Institute of Standards and Science
NIM	National Institute of Metrology (China)
NPL	National Physical Laboratory
NRLM	National Research Laboratory of Metrology (Japan)
MPI	Max Plank Institute (Germany)
OIML	International Organization of Legal Metrology
VSL	Van Swinden Laboratory (Netherlands)

Associations and Committees

AAAR	American Association for Aerosol Research
ACS	American Chemical Society
AGA	American Gas Association
AIAA	American Institute of Astronautics and Aeronautics
AIChE	American Institute of Chemical Engineers
AIRAPT	Int'l Association for the Advancement of High Pressure Science and Technology
API	American Petroleum Institute
ASHRAE	American Society of Heating, Refrigeration, and Air Conditioning Engineers
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
ATCC	American Type Culture Collection
AVS	American Vacuum Society
BIPM	International Bureau of Weights and Measures
BRS	Biotechnology Research Subcommittee
CAALS	Consortium on Automated Analytical Systems
CAP	College of American Pathologists
CARB	Center for Advanced Research in Biotechnology
CEESI	Colorado Engineering Experiment Station, Inc.

CLSH	Committee on Life Science and Health
CSIRO	Commonwealth Scientific and Industrial Research Organization
DIPPR	Design Institute for Physical Properties Data
EPRI	Electric Power Research Institute
FCCSET	Federal Coordinating Committee on Science, Engineering, and Technology
GEC	Gaseous Electronics Conference
GPA	Gas Processors Association
GRI	Gas Research Institute
IAPWS	International Association for the Properties of Water and Steam
ICLASS	International Conference on Liquid Atomization and Spray Systems
ICUMSA	International Commission for Uniform Method of Sugar Analysis
IEA	International Energy Agency
IEEE	Institute of Electronic and Electrical Engineers
IFPAC	International Forum on Process Analytical Chemistry
ISA	Instrument Society of America
ISO	International Organization for Standardization
IUBMB	International Union of Biochemical and Molecular Biology
IUPAC	International Union of Pure and Applied Chemistry
MAS	Microbeam Analysis Society
MRL	Microelectronics Research Lab
NATO	North Atlantic Treaty Organization
NCCLS	National Clinical Chemistry Laboratory Standards
NCSL	National Conference of Standards Laboratories
NHEXAS	National Human Exposure Assessment Survey
SEMATECH	Semiconductor Industry Technology Consortium
SPIE	Society of Photo-optical Instrumentation Engineers
SWRI	Southwest Research Institute
TAC	Technical Advisory Committee
TWGDAM	Technical Working Group on DNA Analysis Method
VAMAS	Versailles Project on Advanced Materials and Standards
WHO	World Health Organization

Technical

1D	One Dimensional
2D	Two Dimensional
AEM	Analytical Electron Microscope
AES	Auger-Electron Spectroscopy
AHERA	Asbestos Hazard Emergency Response Act
AL	Attenuation Length
AMP	Adenosine Monophosphate
AMS	Accelerator Mass Spectrometry
ASEM	Automated Scanning Electron Microscopy/Electron Probe Microscope
amu	Atomic Mass Unit
ANN	Artificial Neural Networks

AP	Alkaline Phosphatase
ATP	Advanced Technology Program
BASIC	Beginner's All-Purpose Symbolic Instruction Code
BGO	Bismuth Germanate
BMCD	Biological Macromolecule Crystallization Database
BR	Bacteriorhodopsin
BSA	Bovine Serum Albumin
C_{18}	Octadecylsilane
CA	Carbonic Anhydrase
cAMP	Cyclic Adenosine Monophosphate
CBWA	Chemical/Biological Warfare Agents
CCD	Charge Coupled Device
CCP	Cytochrome c Peroxidase
CDG	Capacitance Diaphragm Gage
CE	Capillary Electrophoresis
CFC	Chlorofluorocarbon
CFD	Computational Fluid Dynamics
cGMP	Cyclic Guanosine Monophosphate
CHI	Concentration Histogram Imaging
CID	Charge Injection Device
CLS	Classical Least Squares
CMOS	Complementary Metal Oxide Semiconductor
CNPGAA	Cold Neutron Prompt Gamma-ray Activation
CNRF	Cold Neutron Research Facility
COSY	Correlation Spectroscopy Experiment
CO-Hb	Carbon Monoxide-Hemoglobin
CPA	Carboxypeptidase A
CRADA	Cooperative Research and Development Agreement
CRP	Cyclic AMP Receptor Protein
CRT	Cathode Ray Tube
CVD	Chemical Vapor Disposition
DDE	Dynamic Data Exchange
dL	Deciliter (10^{-1} liters)
DLS	Dynamic Light Scattering
DNA	Deoxyribonucleic Acid
DNB	Dinitrobenzene
DSC	Differential Scanning Calorimetry
DTSA	Desktop Spectrum Analyzer
ECL	Electrogenerated Chemiluminescence
ECS	Extended Corresponding States
EDS	Energy Dispersive Spectrometer
EERC	Ejector Expansion Refrigeration Cycle
EMPA	Electron Probe X-Ray Microanalysis
ESEM	Environmental Scanning Electron Microscopy
ESI-MS	Electrospray Ionization Mass Spectrometry
ETAAS	Electrothermal Atomic Absorption Spectrometry

FC	Fluorocarbon
FE-STEM	Field Emission-Scanning Transmission Electron Microscope
FIA	Flow Injection Analysis
FIIA	Flow Injection Immunoassay
FTIR	Fourier Transform Infrared
FTS	Fourier Transform Spectroscopy
FWHM	Full-Width, Half-Maximum
FY	Fiscal Year
GC	Gas Chromatography
GC-ECD	GC with Electron Capture Detection
GC/MS	Gas Chromatography/Mass Spectrometry
GD	Glow Discharge
GST	Glutathione-S-Transferase
H	Hydrogen
HAS	High Accuracy Spectrophotometer
Hb	Hemoglobin
HCFC	Hydrochlorofluorocarbon
HDL	High Density Lipoproteins
HETCOR	Hetero Nuclear Correlation
HFC	Hydrofluorocarbon
HMBC	Hetero Nuclear Multiple Bond Correlation
HMQC	Hetero Nuclear Quantum Correlation
HPEC	High Performance Exclusion Chromatography
HSA	Human Serum Albumin
HTSI	Hadamard Transform Spatial Imaging
HTSPRT	High Temperature Standard Platinum Resistance Thermometer
HVAC	Heating Ventilation and Air Conditioning
ICP	Inductively Coupled Plasma
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ID	Isotope Dilution
IDMS	Isotope Dilution Mass Spectrometry
IFN-γ	Interferon-Gamma
IgG	ImmunoglobulinG
IMFP	Inelastic Mean Free Path
INAA	Instrumental Neutron Activation Analysis
IR	InfraRed
ITS-90	International Temperature Scale of 1990
JP8	Designation for Jet Fuel
KHP	Potassium Hydrogen Phthalate
LADH	Liver Alcohol Dehydrogenase
LC	Liquid Chromatography
LDH	Lactate Dehydrogenase
LDL	Low Density Lipoproteins
LDV	Laser Doppler Velocimetry
LEI	Laser-Enhanced Ionization

LIF	Laser-Induced Fluorescence
LISP	List Processing Computer Language
LLE	Liquid-Liquid Equilibrium
LOX	Liquid Oxygen
Lp(a)	Lipoprotein (a)
MBE	Molecular Beam Epitaxy
MBWR	Modified Benedict-Webb-Rubin Equation of State
MECE	Micellar Electrokinetic Capillary Electrophoresis
mg	Milligram (10^{-3} grams)
MHz	Megahertz
mL	Milliliter
MLx	MacLispix Image Processing Software
MO	Metallorganic
MOCVD	Metallorganic Chemical Vapor Deposition
MRF	Metering Research Facility
MRG	Microanalysis Research Group
MSEL	Materials Science and Engineering Laboratory
MS	Mass Spectrometry
MW	Molecular Weight
NAA	Neutron Activation Analysis
NDP	Neutron Depth Profiling
NIR	Near Infrared
NMR	Nuclear Magnetic Resonance
NSB	Non-Specific Binding
NTI	Negative Thermal Ionization
NVLAP	National Voluntary Accreditation Program
OH	Hydroxyl
OPTR	Orifice Pulse Tube Refrigerator
PAH	Polycyclic Aromatic Hydrocarbons
PC	Personal Computer
PCA	Principle Component Analysis
PCB	Polychlorinated Biphenyl
PCR	Polymerase Chain Reaction
PEELS	Parallel Detection Electron Energy Loss Spectrometry
PGAA	Prompt Gamma Activation Analysis
Pd	Palladium
pH	Measure of the Concentration of Hydrogen Ions
pK	Value of pH for which an Affect is Maximum
PLIF	Planar Laser Induced Fluorescence
PLM	Polarized Light Microscopy
PLS	Partial Least Squares
pM	Picomolar
PPA	Partial Pressure Analyzer
ppb_V	Parts-Per-Billion Volume
ppm	Part Per Million
ppm_V	Parts-Per-Million Volume

PSM	Primary Standard Gas Mixtures
PTS	Phosphotransferase System
PVT	Pressure-Volume-Temperature
PVTx	Pressure-Volume-Temperature-Composition
Rabc	Refrigerant abc
REFPROP	NIST Computer Package for the Properties of Alternative Refrigerants
REMPI	Resonance-enhanced multiphoton ionization
RF	Radio Frequency
RFLP	Restriction Fragment lenLth Polymorphism
RHEED	Reflection High-Energy Electron Diffraction
RIA	Radio Immunoassay
RNA	Ribonucleic Acid
RSF	Relative Sensitivity Factors
SAM	Self-Assembled Monolayers
SAMS	Self-Assembled Monolayers
SANS	Small Angle Neutron Scattering
SAW	Surface Acoustic Wave
SCAPS	Site Characterization and Analysis Penetrometer System
SCWO	Supercritical Water Oxidation
SEM	Scanning Electron Microscopy
SERS	Surface enhanced Raman Spectroscopy
SFC	Supercritical Fluid Chromatography
SFE	Supercritical Fluid Extraction
SHG	Second Harmonic Generation
SIGMA	Supersonic Inert-Gas Metal Atomization
SIMS	Secondary Ion Mass Spectrometry
SPM	Surface Plasmon Microscopy
SPR	Surface Plasmon Resonance
SPRT	Standard Platinum Resistance Thermometer
SRD	Standard Reference Data
SRM	Standard Reference Material
SRP	Standard Reference Photometer
SSME	Space Shuttle Main Engine
STM	Scanning Tunnelling Microscope
SURF	Synchrotron Users Ultraviolet Radiation Facility
TAD	Thermoacoustically Driven
TADOPTR	Thermoacoustically Driven Orifice Pulse Tube Refrigerator
TC	Thermocouple
T_c	Critical Temperature
TCP-IP	Transmission Control Protocol-Internet Protocol
TEA	Triethylamine
TEG	Triethylgallium
TEOS	Tetraethyoxysilane
TG	Triglycerides
TLD	Thermal Luminescence Dosimetry
TLN	Thermolysin

TOCSY	Totally Correlated Spectroscopy
TOF-SIMS	Time-of-Flights Secondary Ion Mass Spectrometer
TQM	Total Quality Management
Trp	Tryptophan
Try	Tyrosine
α-TNF	Antiproliferative Agents Tumor Necrosis Factor
UHV	Ultra High Vacuum
UIM	Ultrasonic Interferometer Manometer
UV	Ultraviolet
UV-VIS	Ultraviolet-Visible (Spectroscopy)
VLE	Vapor-Liquid Equilibrium
VLSI	Very Large Scale Integration
VOC	Volatile Organic Compounds
VRD	Video Radiation Detector
WDS	Wavelength-Dispersive X-Ray Spectrometry
XPS	X-ray Photoelectron Spectroscopy
XRF	X-Ray Fluorescence
ZAF	Quantitative Algorithm