



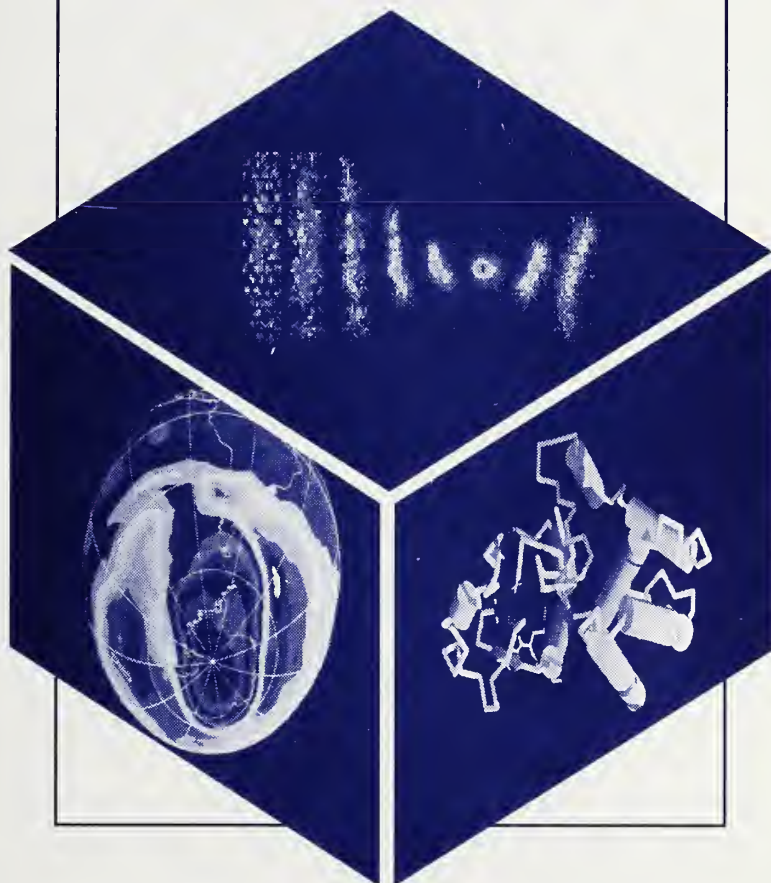
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**Chemical Science and  
Technology Laboratory**

NIST  
PUBLICATIONS

# CSTL Technical Activities 1993



**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

**February 1-2, 1994**

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Shown on the cover (clockwise starting at the top): Images along the neutron beam path at the exit end of a prototype neutron focusing lens, taken with a video radiation detector developed at NIST; A monomer of the three-dimensional structure of Glutathione S-Transferase (GST), a human enzyme produced in the liver and other tissues, whose structure is being studied to help design more effective treatments for cancer; Depiction of stratospheric ozone showing the "hole" in the ozone layer in the region of the south pole. CSTL scientists provide physical and chemical data necessary to model the effects of man-made chemicals on the ozone layer.

**Chemical Science and  
Technology Laboratory**

# **1993 Technical Activities**

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

**February 1-2, 1994**

**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, Undersecretary for Technology  
National Institute of Standards and Technology, Arati Prabhakar, Director**

1992

1993

Technical Analysis

1994

1995

1996



1997

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## Chemical Science and Technology Laboratory

Hratch G. Semerjian, Director

Barry I. Diamondstone, Deputy Director

### A. Program Overview

The expanded responsibilities we were given nearly six years ago in becoming the National Institute of Standards and Technology have provided us with a significant challenge. 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. With these goals in mind, the following comprehensive mission statement was written for the Chemical Science and Technology Laboratory:

- a) provide the national system of chemical and physical measurements; coordinate the system with measurement systems of other nations and furnish essential services leading to accurate and uniform chemical measurements throughout the Nation's scientific community, industry, and commerce; provide advisory and research services to other government agencies; conduct basic and applied research in analytical chemistry, biotechnology, chemical engineering, and physical chemistry; and conduct interdisciplinary research efforts with other NIST laboratories in these areas;
- b) conduct fundamental investigations of the phenomena on which measurement of the composition and behavior of chemical and biochemical systems is based; provide benchmark experimental data, new theory and models to explain the behavior and predict the properties of chemicals in chemical and biochemical processes and systems; develop and certify Standard Reference Materials; produce and evaluate Standard Reference Data; acquire and disseminate thermophysical, thermodynamic, kinetic, and thermal data; provide calibration services for temperature, pressure, vacuum, flow, volume, liquid density, and humidity; develop new laboratory and process measurement techniques, including in-situ real-time process measurement methods;

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NOTE: Certain commercial equipment, instruments, 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.

- c) aid competitiveness in the global marketplace of the diverse U.S. industries that are reliant on generic research and technology development in chemistry and chemical engineering; develop and improve measurement capability and quantitative understanding of basic physical processes that underlie measurement science, including methods for analytical chemistry, biological chemistry, chemical kinetics, thermodynamics, and surface science, and thereby improve comparability among laboratories; use the methods to assist in the solution of problems of national impact, e.g., in improving the accuracy of clinical analytical chemistry, air and water pollution analysis, and chemical engineering metrology.

Our current activities address important areas within the mission of the Chemical Science and Technology Laboratory. Some indicators of success in meeting the expanded responsibilities of our new mission 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 FY93 are summarized in the table below.

Div.	Pubs.	Talks	Committees <sup>1</sup>	Seminars	Conferences	CRADAs	Patents	SRMs	SRD	Cals. <sup>2</sup>
830	3	8	29	8	6	0	0	0	0	0
831	70	93	57	40	9	13	4	0	1	0
833	55	50	45	15	3	1	0	4	6	0
834	96	98	126	8	7	22	1	102	0	172
835	43	61	34	17	6	5	0	42	0	61
836	77	98	93	17	10	33	5	4	1	1023
837	112	128	76	17	4	2	2	6	3	11
838	64	110	68	13	5	1	3	0	5	108
Totals	520	646	528	135	50	77	15	158	16	1375

<sup>1</sup>Committee totals include 55 editorships

<sup>2</sup>Calibrations were performed for over 400 customers

There were many noteworthy accomplishments by CSTL personnel in these areas in FY93, some 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).

*Research* efforts by CSTL scientists in a number of diverse areas have been recognized by their colleagues. Among the outstanding achievements were the measurements of atmospheric kinetics relevant to the depletion of the ozone layer due to trace constituents, particularly ones generated by human activity (833); use of femtosecond laser measurements to discriminate between the energy coupling modes of adsorbates with substrate electrons and phonons (837); completion of comprehensive measurements and data correlation for the thermophysical properties of five alternative refrigerants for the air conditioning and refrigeration industry (838); research on the structure and folding of a genetically engineered subtilisin mutant (831); development of a

technique to photolithographically pattern self-assembled monolayer films with micrometer resolution (836); use of neutron focussing to study capillary optic devices, which generated a new design for a lens to be used for neutron depth profiling and prompt gamma activation analysis that had a factor of 20 gain in intensity and a spatial resolution of  $< 0.5$  mm (834); and the development of an automated flow injection immunoassay (FIIA) device for the measurement of breast cancer markers in human serum (835).

More than 500 *publications* were authored or coauthored by CSTL scientists and over 600 *talks* were presented at local, national and international meetings. A review paper on the unified treatment of the measurement of pressure and vacuum was selected for the prestigious NIST Condon Award, which recognizes distinguished achievement in written exposition in science or technology (838). A paper was published on a new liquid chromatographic phase tailored for the separation of carotenoid compounds, which are a class of organic compounds that may be important for a variety of industrial and health fields (835). A paper on the genetically-engineered calcium independent subtilisin enzyme was featured on the cover of *Proteins: Structure, Function, and Genetics* (831). A paper on our unique neutron depth profiling techniques and facilities was featured on the cover of *Neutron News* (834). Important data needed for the on-line monitoring of GaCl, a transport agent used in etching and chemical vapor deposition (CVD), was published (833). A definitive paper was published in *Analytical Chemistry* on trace analysis describing capabilities for qualitative and quantitative analysis for almost single atoms (837). The premier issue of the *Journal of Neutron Research* featured the work of Division 834 on focussed neutrons and capillary optics. NIST Monograph 175 was published on thermocouple reference functions and tables, which will be the defining document for thermocouple thermometry in industry and calibration laboratories throughout the world (836). Results were published on a breakthrough optical technique for measuring CO in ultrahigh vacuum processes, allowing less intrusive probing of vacuum environments (838).

The number of *CRADAS* and *consortia* have grown significantly in the last few years in response to our expanded role to aid industrial competitiveness. At the end of FY93, the Consortium on Advanced Biosensors, which was established to foster biosensor development and address generic biosensor problems, had 7 CRADAs with industrial members and one Federal agency member (831). A CRADA was established with HiAc-RoyCo to collaborate in developing a particles-in-oil SRM, which will be critical in the power transmission industry (837). A CRADA was established with the Sadtler Division of Bio Rad to develop computer software for an advanced searching system for the mass spectrometry database (833). As part of a CRADA with Babcock and Wilcox, Inc., Division 836 is developing *in-situ* diagnostic measurements of chemicals in high pressure/high temperature water for applications in steam cycle power systems (836). The Consortium for Automated Analytical Laboratory Systems (CAALS) made excellent progress in producing the first standards-in-communication protocol between various components which make up an analytical system (834). Through a CRADA with DH Instruments, a manufacturer of pressure gages, a new type of gas-operated deadweight piston gage has been developed whose uncertainty in pressure measurement is competitive with mercury manometers (838). A CRADA to further the development of the automated device for

detection of breast cancer markers was established with Paracelsian to couple NIST's expertise in FIIA with the company's expertise in antibody preparation, purification, and instrumentation design (835).

In FY93, CSTL scientists received *patents* for an apparatus and method for evaporative concentration of a liquid sample (838), and a method for bonding thin-film thermocouples to ceramics (836). The invention of the desktop spectrum analyzer and X-ray database was allowed (patent imminent) by the patent office (837). Among the more significant invention disclosures or patent pending applications were an improved high temperature vibrating tube densimeter (838), a method for photoelectrochemical detection of carcinogens by DNA intercalation (831), and ultraviolet photopatterning of self-assembled monolayers on gold and silver (836).

*Measurement services* remain a high priority in CSTL. Nearly 160 *SRMs* were certified for chemical composition or physical properties. Examples of important work in this area include the certification of organic contaminants (PCB congeners and chlorinated pesticides) in whale blubber (835); a depth profile standard for boron implanted in silicon (837, 834); the certification of four *SRMs* on the heating value of sulfur-containing coals (833); the certification of a catalyst material for automobile exhaust (834); and the certification of a freezing-point standard for silver (836). 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, temperature, and volume measurements (836); re-calibration of gas concentrations for gas cylinders (835); optical filter transmission for absorption spectrophotometers (834); and pressure and leak rate measurements (838). This year, two additional standard reference photometers for ozone measurement were built (837); a facility was completed for calibration of thermometers in the 0.65 to 84 K range (836); and a new spinning rotor gage controller was developed for vacuum measurement that has significant advantages over commercially-built controllers (838). Among the significant *SRDs* issued were the Notre Dame Research Laboratory/NIST liquid phase kinetics database (833), an update of the NIST/NASA/CARB biological macromolecule crystallization database (831), and a new version of REFPROP, which provides thermophysical properties of pure refrigerants and mixtures (838).

CSTL scientists utilized *conferences and workshops* to assess industrial research and development areas where NIST could make a significant contribution. In September, our staff held a workshop on gas sensors and strategies for future technologies (836). Thermophysics Division staff co-organized the NATO Advanced Summer Institute on Supercritical Fluids, held in July. Division 835 held a workshop on the standards needs for reformulated fuels. Our staff sponsored the NIST/ASTM Workshop on Standardization Needs in Biotechnology (831). In July, Division 833 staff organized the Third International Conference on *Chemical Kinetics: Reactions in Gas and Condensed Media*. The Workshop on Technology Requirements for Environmental Management was co-chaired by CSTL and the Physics Laboratory staff. A landmark meeting was held between ISO and IUPAC in July (837 staff serving as the focal point), to establish the groundwork for detection decisions and detection limits in chemical and



physical metrology. The Process Measurements Division (836) held two workshops on waste minimization to formulate a role in industrial waste avoidance and treatment. CSTL held a workshop with the EPA in July to identify areas of joint interest and collaborative research in environmental technologies.

CSTL staff participated in *external activities* to assist other government or industrial organizations. Staff served on two Federal Coordinating Committee on Science, Engineering, and Technology (FCCSET) subcommittees: Biotechnology Research and Environmental Technology. These committees have the charge of coordinating research in the Federal government in their appropriate area, providing recommendations for commercial implementation of new or existing technologies, and identifying appropriate technology research needs. L. Powell (831) is the Chair of the Biotechnology Research Subcommittee (BRS), and Biotechnology Division staff chair the BRS working groups on bioprocessing and technology transfer. CSTL staff participated on the Interagency Environmental Technologies Exports Working Group, which culminated in a report to the President proposing a strategy to enhance exports of U.S. environmental technologies. W. Koch (834) was elected to the Board of Directors of the National Committee for Clinical Laboratory Standards. Under the leadership of M. McLinden (838), the Thermophysics Division serves as the operating agent for a project entitled "Thermophysical Properties of the Environmentally Acceptable Refrigerants" under the auspices of the International Energy Agency. The National Human Exposure Assessment Survey (NHEXAS) is a long-term program to measure changes in individual human exposures to important environmental pollutants for a "representative" sample of the U.S. population; W. May (835) serves on the Federal Interagency Coordinating Committee for the project. R. Fletcher (837) collaborated with the National Fluid Power Association on developing international standards for particles-in-oil. M. Kurylo (833) is the Chairman of the International Scientific Steering Committee of the Network for the Detection of Stratospheric Change. The Semiconductor Industries Roadmap Planning Workshop was held in November, 1992 and J. Whetstone (836) served on the Equipment Modeling and Design working group. The CSTL Director presented testimony to the Subcommittee on Technology, Environment, and Aviation of the U.S. House of Representatives on NIST activities in developing measurement methods and reference materials regarding lead pollution in the environment. This was part of a hearing on the role of NIST in U.S. technology policy, held at NIST in July of 1993.

Several CSTL scientists received *awards* and recognition for outstanding achievements in FY93. These included the presentation of the Department of Commerce *Silver Medal* to M. Dizdaroglu for contributions to the development and application of methods aimed at understanding the role of DNA damage in the genesis of disease; the Department of Commerce *Bronze Medal* to A. Miiller for developing a high-speed laser interferometric technique for measuring thermal expansion of electrically conducting solid materials at high temperatures; the Department of Commerce *Bronze Medal* to M. Zachariah for chemical engineering research in the processing of high-technology materials via multiphase chemical reactions; the NIST *Applied Research Award* to L. Brown and S. Choquette for their unusual creativity in the conceptualization, development, and critical evaluation of a flow-injection immunoassay device for measurement

of breast cancer markers in human serum; the NIST *Condon* Award to C. Tilford for a review paper of pressure and vacuum instrumentation; the NIST *Rosa* Award to D. Reeder and K. Richie for developing and certifying the DNA profiling Standard Reference Material; the NIST *Equal Employment Opportunity* Award to W. May for addressing concerns regarding the under-representation of minorities at NIST; the NIST *Slichter* Award to P. Espina and G. Mattingly for efforts as part of the industry/NIST SIGMA consortium; and NIST *Measurement Services* Awards to D. Friend (fluid mixture data center), W. Mallard (chemical kinetics database), M. Schantz (trace organic analysis), M. Smith (optical filter SRM), S. Stein (mass spectral and vapor phase IR databases), and W. Tew (low temperature calibrations). External awards to CSTL scientists included: an *R&D 100* Award to D. Reeder and K. Richie for the DNA profiling SRM; the *Top Science Award in the Basic Sciences* from the Republic of Turkey to M. Dizdaroglu for the role of DNA damage in the genesis of disease; election as the first *President of the International Society of Polycyclic Aromatic Compounds* to W. May; Department of Commerce *Engineer of the Year* Award to G. Mattingly for the development of measurement technology, standards, and calibrations services for fluid flow; the *15-Year Appreciation* Award of the International Cryocooler Conference to R. Radebaugh for contributions and dedication in promoting cryocooler technology; ASTM Committee E-42 award named for C. Powell, to be given to a person for outstanding contributions to standards for surface analysis; the *Microbeam Analysis Society (MAS) Presidential* Award to D. Newbury for outstanding contributions to the theory and practice of microbeam analysis; election of C. Fiori posthumously as an honorary member of the MAS for scientific contributions to microanalysis; election to *Fellow of the Acoustical Society of America* to M. Moldover for outstanding experimental contributions in critical phenomena, interfacial phenomena, and acoustic metrology, including a more accurate determination of the Universal Gas Constant; and an *ASME Award for Vision and Leadership* in the field of utility and steam generation to J.M.H. Levelt Sengers.

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**

Avedisian, C.T., Presser, C., Gupta, A.K., and Semerjian, H.G., "Observations of Soot in Combustion of Methanol/Toulene Spray Flames," in General Papers in Heat Transfer and Heat Transfer in Hazardous Waste Processing, (A.S. Lavine, M.K. Jensen, R.L. Mahajan, E.V. McAssey, M.F. Modest, D.W. Pepper, C. Presser, R.D. Skocypec, and M.S. Sohal, Eds.), HTD-212, 161-167, ASME, NY (1992).

Hodges, J.T., Gréhan G., Presser, C., and Semerjian, H.G., "Elastic Scattering from Spheres Under Non-Plane Wave Illumination," in Laser Applications in Combustion and Combustion Diagnostics 1862 (L.C. Liou, Ed.), SPIE-The Int'l Society for Optical Engineering, Bellingham, WA, 294-308 (1993).

Presser, C., Gupta, A.K., and Semerjian, H.G., "Aerodynamic Characteristics of Swirling Spray Flames: Pressure-Jet Atomizer," *Combustion and Flame* 92, 25-44 (1993).

**2. Talks**

Diamondstone, B.I., "Advanced Technology Program at NIST," DIR-AG Meeting, Minneapolis-St. Paul, MN, May 12-14, 1993.

Semerjian, H.G., "Environmental Technologies at NIST", Environmental Tech Transfer '92, November 10, 1992.

Semerjian, H.G., "Environmental Management through Chemical Metrology", Conference on Metrology for Environmental Management, April 14, 1993.

Semerjian, H.G., "Environmental Technologies in NIST", NIST/NOAA Workshop on Environmental Technologies, NIST Gaithersburg, MD, April 26, 1993.

Semerjian, H.G., "Environmental Technologies at NIST", EPA/NIST Workshop, Cincinnati, OH, July 14, 1993.

Semerjian, H.G., "Environmental Technologies - NIST Strategic Plan", Workshop on Identification of Critical Measurement Needs for Waste Minimization in Industrial Processes, NIST Gaithersburg, MD, September 15, 1993.

Semerjian, H.G., "Measurement Methods and Reference Materials Regarding Lead Pollution in the Environment", Hearing Before the U.S. House of Representatives Subcommittee on Technology, Environment, and Aviation on the Role of NIST in U.S Technology Policy, NIST Gaithersburg, MD, July 26, 1993.

Semerjian, H.G., "Environmental Standards to Improve Quality Control", ENVIROMEX '93 Conference, Monterrey, Mexico, September 22, 1993.

### 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 for Chemical Research  
Directors of Industrial Research - Analytical Group

#### **S. Dittmann**

CSTL Colloquium Committee (Chair)

#### **M. S. Epstein**

National Capital Area Skeptics, Board of Directors (Vice President)  
EPA Working Committee on Lead-Based Paint Good Lab Practices Guide  
Society for Scientific Exploration Annual Meeting, Program Committee  
National Committee for Clinical Laboratory Standards, Subcommittee on Control of Proanalytical Variation in Trace Metal Analysis  
Society for Scientific Exploration, Governing Council  
Montgomery Area Science Fair (1993) (Judge)  
CSTL Electronic Notebook Policy Committee (Chairman)

#### **D.A. Olson**

Boulder Editorial Review Board  
CSTL Colloquium Committee

#### **H.G. Semerjian**

Combustion Institute - 24th Symposium (International) on Combustion, Program Subcommittee  
ASME K-11 Committee on Heat Transfer on Fires and Combustion Systems

AIChE Engineering Sciences and Fundamental Group, Area 1b. - Kinetics, Catalysis and Reaction Engineering  
AIChE Food, Pharmaceutical and Bioengineering Division, Area 15C - Biotechnology  
International Conference on Liquid Atomization and Spray Systems  
ICLASS-94 - Organizing Committee  
Council for Chemical Research  
- Committee on Science Education  
- 1994 Program Committee  
- University - Industry - Government Interaction Committee  
Directors of Industrial Research - Analytical Group  
Interagency Working Group on Environmental Technologies  
FCCSET Subcommittee on Environmental Technologies

#### 4. Editorship

##### M.S. Epstein

Editorial Advisory Board, Journal of Analytical Atomic Spectroscopy  
Column Editor, Journal of Scientific Exploration  
Editor, CSTL Update Newsletter

#### 5. Laboratory Colloquium Series

##### October 7, 1992

Robert R. VanDuyne, Northwestern University, Evanston, IL, "Surface Laser Spectroscopy: Hyper-Raman, Nanostructure, and Epitaxial Layers."

##### December 10, 1993

Helen Free, Miles Laboratories, Elkhart, IN, "The American Chemical Society: What's in it for NIST."

##### January 22, 1993

Mark J. Kushner, Department of Electrical and Computer Engineering, University of Illinois, Urbana, IL, "Two Problems in Plasma Processing: Selective Chemistry and Particles."

##### February 10, 1993

Michael R. Moldover, Thermophysics Division, NIST, Gaithersburg, MD, "Acoustic Measurements of Thermophysical Properties."

**March 18, 1993**

David B. Frazier, Manager, Thin Films Research, Intel Corporation, Santa Clara, CA,  
"Metrology Issues in Semiconductor Processing."

**April 14, 1993**

Kermit C. Smyth, Building and Fire Research Laboratory, NIST, Gaithersburg, MD,  
"Laser Studies of Steady-State and Time-Varying Diffusion Flames."

**May 19, 1993**

Dennis J. Reeder, Biotechnology Division, NIST, Gaithersburg, MD, "Forensic DNA  
Profiling."

**June 16, 1993**

J. William Gadzuk, Surface and Microanalysis Division, NIST, Gaithersburg, MD, "Hot  
Electrons: The Key to FemtoChemistry."

**6. Conferences/Workshops Sponsored/Co-Sponsored**

**October 21-23, 1992**

13th Annual Meeting of the Analytical Laboratory Managers Association (ALMA), New  
Orleans, LA (B. Diamondstone)

**November 1-6, 1992**

Combustion Reacting Engineering, American Institute of Chemical Engineers (AIChE),  
1992 Annual Meeting, Miami Beach, FL (H. Semerjian)

**April 14-15, 1993**

NIST/DoD/DoE/DoT Conference on Metrology for Environmental Management, NIST,  
Gaithersburg, MD (B. Watters)

**April 26, 1993**

NIST/NOAA Workshop on Environmental Technologies, NIST, Gaithersburg, MD (H.  
Semerjian)

**June 30, 1993**

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

**July 14, 1993**

EPA/NIST Workshop, Cincinnati, OH (H. Semerjian)

## 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. During FY93, the Division has been involved in a number of activities which will assist the private sector in commercializing biotechnology research. The Division has continued interactions with the two primary Biotechnology trade organizations, the Association of Biotechnology Companies (ABC) and the Industrial Biotechnology Association (IBA). In July 1993, these two trade organizations merged to become the Biotechnology Industry Organization (BIO). The Division, which was a member of the ABC, continues its interactions as a member of BIO. The Division actively participates with the ASTM Committee E-48 on Biotechnology. Division members serve as 1st Vice Chair of the committee and as Chair of the Subcommittee on Terminology and participate as members on other subcommittees. In April 1993 the Division cosponsored with ASTM the Workshop on Standardization Needs in Biotechnology. The workshop, which was held at NIST, attracted more than a hundred representatives from industry, government, and academe and resulted in the identification of more than 90 standards that need development. During FY93, the Division also cosponsored the workshops "Biotechnology Applications in Biomaterials" in April 1993 and "Frontiers in Bioprocessing III" in September 1993. The Division cosponsored and hosted the 1st International Conference on Bioelectronics and Biocomputing at NIST in September 1993.

During FY92, the Division initiated an effort to form a consortium to address the needs of the biosensor industry. On April 15, 1993, the Consortium on Advanced Biosensors (CAB) became official. By the end of FY93, CAB had 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. During FY93, the Division executed nine new Cooperative Research and Development Agreements (CRADAs), including seven associated with CAB, in addition to the two CRADAs which were continued from FY92. Several other CRADAs are under negotiation. The Division also filed four patent disclosures during the year.

Last year NIST completed its first biotechnology Standard Reference Material (SRM), a DNA profiling quality assurance kit to assure the accuracy of DNA measurements in forensic and paternity testing. In September 1993, the SRM was recognized by R&D Magazine as one of the top 100 new products of the year and NIST, along with its industrial collaborators on the project, received an R&D 100 award.

The Biotechnology Division continued to play a major role in the Biotechnology Research Subcommittee (BRS) of the Federal Coordinating Committee on Science, Engineering, and Technology (FCCSET) Committee on Life Science and Health (CLSH). The BRS has the long-term charge of coordinating biotechnology research throughout the Federal government and providing recommendations on areas of opportunity for the future. Biotechnology was again chosen as a Presidential Initiative for FY94. The BRS developed the report, "Biotechnology in the 21st Century: Realizing the Promise" which includes recommendations for biotechnology research which fit very well with NIST priorities for its biotechnology program. In July 1993, the Chair of the BRS announced his departure from the Federal government and Dr. Lura Powell, NIST, was asked to take his place. NIST Biotechnology Division staff Chaired the Bioprocessing and Technology Transfer Working Groups. NIST also participated in the Working Group on Structural Biology. As a result of this involvement, NIST Biotechnology research, while representing only 0.1% of the total Federal investment in biotechnology research, is well represented in the BRS report and its recommendations, and collaborations with other agencies have resulted.

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. As with all NIST programs, a major emphasis of the NIST biotechnology program is to provide advisory and research services to industry, other government agencies and the scientific community. The Biotechnology Division is organized into four Groups: (1) the Biochemical Measurements Group's activities are focussed on separation, modification, immobilization and stabilization of biomolecules and mechanisms of DNA damage and repair; (2) the Biophysical Measurements Group's activities focus on biothermodynamics and transport processes of biomolecules; (3) Center for Advanced Research in Biotechnology (CARB), whose activities focus on the understanding of protein structure/function and energetics (CARB is a joint venture with the University of Maryland and Montgomery County, Maryland); and (4) Biosensor Technology whose activities focus on development of advanced biosensing devices and biomolecular electronics.

The primary research efforts of the Biotechnology Division are focused on the following areas:

#### DNA and Protein Chemistry/ Standards Development

**DNA Profiling:** Methods and standards are being developed to accurately characterize DNA profiles for forensic and other uses. A standard reference material for quality control and standardization of forensic DNA testing was completed last year. Research is being conducted to develop the next generation of DNA profiling based on polymerase chain reaction (PCR) technology including developing new methods for rapid DNA extraction, amplification, separation, and computer imaging.



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.

Protein Mapping: 2-D electrophoresis, computer imaging and computational techniques are being applied to mapping of proteins in complex systems, including those of living tissues subjected to disease and treatments.

### Bioprocess Engineering

Separation and Purification: Methodologies and the data necessary for their evaluation are being developed to affect the efficient separation and purification of products from their mother liquors.

Design Properties: Thermophysical, thermochemical and engineering properties are being obtained, evaluated, codified and modeled for ubiquitous biochemicals, biosystems and protein solutions of interest to biotechnology. These data will be used by bioengineers to optimize existing processes and to evaluate proposed processes.

### Biosensor Technologies

Sensor Technologies: NIST develops generic sensor technologies utilizing both optical and electrochemical approaches for applications in clinical laboratories, bioprocessing and environmental monitoring.

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

Consortium for Advanced Biosensors (CAB): The Consortium was formed to solve generic problems which prevent the commercialization of many biosensor technologies. The research programs are chosen by the Consortium members and supported through yearly membership fees.

### Protein Engineering (Structural Biology)

Structure/Function/Energetics Relationships: NIST is actively working to understand these relationships using the methods of protein crystallography, molecular biology, biothermodynamics, and computational chemistry and modeling.

**Protein Crystallography:** Active programs are underway to obtain the protein structure of prototypical proteins, enzymes, enzyme-substrate complexes and model DNA systems using X-ray and NMR techniques. Other efforts include the development of a machine readable database for protein crystallization and the development of artificial intelligence techniques for interfacing laboratory robots for protein crystallization studies with the database.

**Protein Folding:** Computational and experimental methods have been developed to determine the thermodynamics, cooperativity and other parameters describing the energetics of protein folding.

**Computational Chemistry and Modeling:** Quantum mechanical formalisms involving reaction fields are being developed to model the energetics and dynamics of interactions between substrates and active sites of enzymes. Modeling techniques to understand the relationship between protein sequence and structure are being developed.

Several Division staff members received awards over the past year. Dr. Dennis Reeder and Ms. Kristy Richie received an R&D 100 award for the development of SRM 2390, DNA Profiling Standard. They were also chosen by the NIST Director to receive the Edward Bennett Rosa Award which recognizes "...outstanding achievements in the development of meaningful and significant standards of practice in the measurement field" for their accomplishments associated with SRM 2390. Dr. Miral Dizdaroglu received the top science award in the basic sciences from the Republic of Turkey in September 1993. Dr. Dizdaroglu was honored for his research in elucidating the mechanism of DNA damage caused by free radicals, which is implicated in the development of cancer and is suspected to be an important part of aging and the development of some diseases. Dr. Dizdaroglu also received a NIST Silver Medal Award this year for these outstanding research efforts.

### Future Directions

Future thrusts of the Biotechnology Division program include expanded efforts in structural biology, bioprocess engineering, DNA separations and standards development, and new programs in biomolecular electronics, biomimetic chemistry and the spectroscopic studies of biomolecular systems. Plans have been developed for program expansions in biosensor technology, biomaterials, upstream and downstream bioprocessing, quality assurance of biotechnology measurements, and protein engineering technology. In addition, plans were developed for a major NIST-wide NMR facility. These plans fit well with the recommendations of the Presidential Initiative in Biotechnology.

During FY93, plans were developed to initiate a new research effort in the development of quality assurance methods and materials for DNA sequencing. During FY94 resources will be directed toward this new research area.

The Division's biomolecular electronics effort received a major boost with the arrival of two Russian guest scientists, N. Vsevolodov and T. Dyukova, who are world leaders in the technology. The expertise that these scientists have brought with them will be invaluable as NIST continues to build a program in this cutting edge technology.

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 1996. An interim expansion, CARB-IB (20,000 square feet), will provide laboratory and office space for 11 additional tenure-track faculty and will include a high field NMR facility. The design phase of this expansion is underway and occupancy is expected in late 1994. 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. Physicochemical Characterization of Low Molecular Weight Heparin**

**D.H. Atha, B. Coxon, V. Reipa (Lithuanian Academy of Sciences, Institute of Chemistry, Vilnius, Lithuania), and A.K. Gaigalas**

Heparin is a sulfated polysaccharide in wide use as an effective anticoagulant and antithrombotic drug. Low molecular weight preparations of heparin are currently being evaluated by the FDA for license in the U.S. as new drugs. In collaboration with the U.S. Pharmacopeial Convention, Inc., a Standard Reference Low Molecular Weight Heparin is under development and is to be used in the quality assurance of these drugs. This required the development of new methods for characterizing these materials.

Nuclear magnetic resonance (NMR) spectroscopy, Raman spectroscopy, dynamic light scattering (DLS) and high performance exclusion chromatography (HPEC) were used to characterize two different commercial preparations of low molecular weight heparin, produced either by peroxide cleavage or deaminative cleavage using nitrous acid. Proton NMR showed that the contamination by dermatan sulfate varied from 2% in the material produced by deaminative cleavage using nitrous acid to 4% for the material produced by peroxide cleavage. The Raman spectra of the nitrous acid-produced material showed an equivalent amount of *O*-sulfation to that in the material produced by peroxide, but about a 10% reduction in the content of *N*-sulfated glucosamine, as expected from the deamination reaction. DLS and HPEC indicated the presence of < 0.2% of very high molecular weight/aggregate material for the peroxide preparation as compared to 1% for the nitrous acid prepared material. The weight average molecular weight ( $M_w$ ) determined from HPEC was 5900 Da for the nitrous acid prepared material and 6850 Da for the peroxide produced material. The number average molecular weight ( $M_n$ ) calculated from this data was 5200 Da for the nitrous acid preparation and 5300 Da for the peroxide produced material. In addition, the nitrous acid prepared material exhibited a much narrower size distribution of oligomeric species, as evidenced by the polydispersity ( $M_w/M_n$ ) of 1.1 for the nitrous acid prepared material, as compared with a value of 1.3 for the peroxide prepared material.

At this time, the Food and Drug Administration is evaluating several low molecular weight heparins for clinical use. NIST will await FDA approval of a particular heparin material before proceeding with certification of a Standard Reference Material.

## 2. Separation of Proteins and Other Solutes by Electrochromatography: Experimental Investigation, Column Design, and Mathematical Modeling

K.D. Cole and H. Cabezas, Jr. (University of Arizona)

Electrochromatography is the application of an electrical field to a bed or column packed with chromatography beads. Proteins are eluted from the bed by a combination of an electrical field and pressure driven convection. Electrophoresis in free solution is not widely used on a preparative scale to purify proteins because of the difficulties in preventing mixing of separated zones by thermal convection. Electrophoresis in a packed bed, however, prevents thermal mixing and offers high capacity. Very selective separations can be achieved by: (1) altering the relative strength of the convection and the electrical field, (2) changing the polarity of the electrical field so that convection and electrophoresis oppose, and (3) altering the chemical and physical properties of the packed bed by changing chromatographic media. Work conducted thus far indicates that by careful manipulation of column conditions and media, electrochromatography may be capable of industrial scale separation of proteins at near analytic resolutions.

Free solution electrophoretic mobilities of several model proteins were measured in columns stabilized by density gradients. The electrophoretic mobility of proteins is an important physical property that can be used as the basis for a separation. Several electrochromatography column designs have been constructed using dialysis membranes to isolate the electrodes from the beds packed with the chromatography media, Sephadex. Preliminary data indicate that axially short and radially wide columns may be optimal for fine protein separations. The elution behavior of bovine serum albumin,  $\beta$ -lactoglobulin A and B,  $\alpha$ -lactalbumin and myoglobin at electric fields around 18 volts/cm and at several flow rates in the creep-flow regime have been studied. The elution behavior of the above model proteins was also studied on Sephadex with a high degree of cross linking (Sephadex G-25) and with a lower amount of cross-linking (Sephadex G-75). It was confirmed that proteins exhibit a still unexplained electrically driven retention on a column packed with Sephadex G-75. The electrically driven retention effect was much reduced or absent in columns packed with the more highly cross-linked Sephadex G-25. The potential of electrochromatography for high resolution separations was demonstrated by the partial separation of  $\beta$ -lactoglobulin A and B in short columns with the electric field oriented such that electrophoresis opposes convective flow.  $\beta$ -lactoglobulin A and B are two nearly identical genetic variants that differ in electrophoretic mobility only by about 8%.

At present, a first generation phenomenological model has been developed for the elution behavior of the aforementioned model proteins in gel filtration columns in the presence and absence of an electrical field. The model predicts elution time and peak dispersion in the columns to near experimental uncertainty. In the absence of an electrical field the model requires no adjustable parameters, while in the presence of a field the model requires one adjustable parameter to characterize the electrically driven retention. A second generation model which includes a more detailed description of the geometry of the medium inside the column is currently under development.

In addition to its application in bioseparations, electrochromatography is being explored to separate, concentrate, and perhaps classify contaminants from polluted streams. For example, charged metal ions which are sensitive to the electric field could be separated from neutral organics and could be made to adsorb on a suitable chromatography media. Chromatography is almost a natural means of concentrating solutes. Applications in both remediation and recycling from existing industrial process streams are anticipated.

3. **Protein Modulation in Human Melanoma Induced by Interferon-gamma and Tumor Necrosis Factor: Two-Dimensional Gel Electrophoresis and Image Analysis**

J.J. Edwards and D.J. Reeder

The molecular events which occur during progression of normal cells to cells exhibiting neoplastic characteristics are of primary importance to our understanding of human cancer. The malignant transformation of human cells is followed by the expression of proteins that differ qualitatively and quantitatively from normal. Newly expressed proteins or those expressed at higher than normal levels are potential markers of genetic products directly linked to the phenotype of the transformed cell. Identification and analysis of these molecular events are essential to the understanding of human cancer. Our studies have focused on mapping, describing, and evaluating *in vitro* protein modulation following treatment of melanoma cells with the antiproliferative agents tumor necrosis factor ( $\alpha$ -TNF) and interferon-gamma (IFN- $\gamma$ ), cytokines that are produced normally in an immune response. Using UCLA-S0 M14 melanoma cells, we found that  $\alpha$ -TNF and IFN- $\gamma$  reduced the cell growth of the malignant cells by 30% and 57% respectively. When used in combination, the synergistic effect resulted in a 90% decrease in growth rate. Of the 900-1000 protein "spots" ranging between 15,000 and 200,000 daltons that could be resolved on the maps, the expression level of 25 proteins were considerably altered. Five proteins were found in the untreated cells that were quantitatively increased over five-fold compared to the treated cells. Likewise, three proteins in the treated samples were found to decrease more than two-fold when compared to the untreated cells. Following treatment with the combination of  $\alpha$ -TNF and IFN- $\gamma$ , two new proteins appeared and five proteins disappeared when compared to the untreated cells. We are continuing to study these modulated proteins as candidates for potential tumor markers and as a method to monitor therapy. This work was in collaboration with D.S.B. Hoon and D.L. Morton of the John Wayne Cancer Institute, Santa Monica, CA.

#### **4. Development of Prototype SRM for PCR-based Technologies for Human Identification**

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

Recently developed techniques in molecular biology are now being applied to human identification cases in forensics and paternity. These procedures, based on the polymerase chain reaction (PCR), allow amplification of very small amounts of DNA recovered from crime scenes. Standards are required for assuring that genetic systems are being properly used and that genetic types are properly identified. To address these needs, a prototype set of materials was developed this year and, after extensive analysis using twelve different electrophoretic gel systems at NIST, the set was sent to twenty-six laboratories in June, 1993. Fifteen laboratories responded with results. Data analysis and evaluation of protocols is still in progress. Preliminary analysis resulted in the identification of several electrophoretic research issues to be resolved. Experiments to address those issues commenced in August, 1993. Further, an experimental design for future interlaboratory tests is being developed from data obtained from the first interlaboratory test. Validation of shipping protocols, use of amplified DNA samples, electrophoretic separation protocols, DNA extraction from blood stains, and PCR amplification sensitivity will be studied in an October 1993 interlaboratory test.

#### **5. Comparison of Isotopic Detection and Chemiluminescence Results for Standard Reference Material 2390, DNA Profiling Standard**

**K.L. Richie and D.J. Reeder**

Until recently, the primary method of detection for Restriction Fragment Length Polymorphisms was through the use of radioactively labeled probes. Isotopic detection, while known for its high degree of sensitivity, can be a time consuming process, often requiring several days for analysis. Moreover, the hazards of using phosphorus ( $P^{32}$ ) labeled probes and the expense involved are major concerns. Therefore, it is not surprising that over the past few years much effort has been spent in developing a detection system that uses non-isotopic techniques which are fast, simple and most importantly as sensitive as those used in isotopic detection methods.

Chemiluminescence generally employs alkaline phosphatase (AP) conjugated DNA probes which hybridize specifically to distinct loci in the sample. Various studies have shown that AP-labeled probes in a chemiluminescent system detect the same locus as equivalent probes labeled with  $P^{32}$  and approach a comparable degree of sensitivity. While it is generally accepted as fact that there are no substantial differences in the sizes of the detected loci, there has been no reported comparison of  $P^{32}$  with chemiluminescence on a standard set of samples. The purpose of the study was to compare isotopic results with chemiluminescence results on Standard Reference Material 2390, a set of well-characterized DNA standards that has been certified by extensive interlaboratory comparisons. Two non-isotopic detection systems were examined. The loci tested were D1S7, D4S139 and D2S44. For both methods there was good correlation between

sizing and results demonstrating that all band sizes were within the stated uncertainties on the SRM certificate.

## 6. Thermodynamic and NMR Study of the Reactions of Cyclodextrins with Cyclohexane Derivatives

M.V. Rekharsky (Lamansov Moscow State University, Chemistry Department, Moscow, Russia), F.P. Schwarz, Y.B. Tewari, R.N. Goldberg, M. Tanaka (Department of Applied Chemistry, Osaka, Japan), and Y. Yamashoji (Department of Applied Chemistry, Osaka, Japan)

This study was undertaken to gain an improved understanding of model substances to cyclodextrins which play a major role in separation technology and drug delivery systems. Equilibrium constants and standard molar enthalpies of reaction have been determined by titration calorimetry for a series of cyclohexane derivatives with  $\alpha$ -cyclodextrin and  $\beta$ -cyclodextrin. The equilibrium constants for the reactions of these substances with  $\beta$ -cyclodextrin are in all cases larger than the corresponding reactions with  $\alpha$ -cyclodextrin. It was also found that the equilibrium constants for the reactions of these substances with  $\gamma$ -cyclodextrin were  $< 4$ . An important feature of these reactions is that, while the standard molar enthalpies of reaction are approximately the same for the reactions with both cyclodextrins, the standard molar entropy changes for the reactions of these substances with  $\beta$ -cyclodextrin are substantially more positive than for the reactions with  $\alpha$ -cyclodextrin. The hydrophilic nature of the groups on the cyclohexane ring as well as steric effects were found to influence the thermodynamics of these reactions. The standard molar enthalpy of transfer of the cyclohexane derivatives from the  $\alpha$ -cyclodextrin complex to the  $\beta$ -cyclodextrin complex was a linear function of the standard molar entropy change for this same transfer reaction. The NMR results indicate a deeper penetration of the cyclohexane derivatives into the  $\beta$ -cyclodextrin than into the  $\alpha$ -cyclodextrin cavity. They also confirm that the cyclohexane derivatives are bound more tightly by  $\beta$ -cyclodextrin and that there is only a negligible interaction with  $\gamma$ -cyclodextrin.

## 7. Surface Enhanced Raman Spectroscopy of Biological Molecules

A.K. Gaigalas, V. Silin (Institute of Biochemistry, Vilnius, Lithuania), and V. Reipa (Institute of Chemical Technology, Vilnius, Lithuania)

Surface Enhanced Raman Spectra (SERS) were recorded for hemoglobin proteins adsorbed on silver electrodes. The excitation wavelength of 514 nm leads to resonant Raman spectrum from the region of the protein containing the heme group. Vibration states were identified which show a reversible shift in wavenumber with reduction and oxidation of the hemoglobin via electrons from the electrode. Spin marker states, which show a shift upon change of the iron spin state, were also identified. The behavior of the redox and spin marker states with electrode potential



provide unique information about electron transfer from the iron site in the protein to the electrode. SERS resonance spectra were obtained for azurin, a copper containing protein, adsorbed on silver electrode. Both of these studies are part of the more general study of electron transfer between proteins and metal electrodes.

SERS and second harmonic generation (SHG) measurements were carried out on the organometallic molecule (E)-1-Ferrocenyl-2-(1-methyl-4-pyridiniumyl)ethylene adsorbed on silver surface of echellete grating. The SHG signal was obtained in the direction of the  $n=-1$  diffraction order. SHG identifies the major electron pathways between donor sites (ferrocene) and acceptor sites (amino group), while SERS determines the nuclear backbone associated with the electron pathway. The combination of techniques could be useful in tracing electronic pathways between metal containing proteins and electrodes.

Measurements were carried out on SERS of pyridine from holographic gratings on a silver surface. The gratings were designed for efficient excitation of surface plasmons with the objective to enhance surface spectroscopy. The excitation of plasmons enhanced the SERS of pyridine about three times. Additional vibrational bands were observed as pyridine concentration was increased.

#### **8. An Equilibrium and Calorimetric Investigation of the Hydrolysis of L-Tryptophan to (Indole + Pyruvate + Ammonia): Calculation of Standard Formation Properties of Reactants and Products**

**Y.B. Tewari and R.N. Goldberg**

Apparent equilibrium constants and calorimetric enthalpies of reaction have been measured for the reaction  $\text{L-tryptophan(aq)} + \text{H}_2\text{O(l)} = \text{indole(aq)} + \text{pyruvate(aq)} + \text{ammonia(aq)}$  which is catalyzed by L-tryptophanase. High-pressure liquid-chromatography and microcalorimetry were used to perform these measurements. The equilibrium measurements were performed as a function of pH, temperature, and ionic strength. The results have been interpreted with a chemical equilibrium model to obtain thermodynamic quantities for the reference reaction:  $\text{L-tryptophan(aq)} + \text{H}_2\text{O(l)} = \text{indole(aq)} + \text{pyruvate}^-(\text{aq}) + \text{NH}_4^+(\text{aq})$ . These results have been used together with thermodynamic results from the literature to calculate standard Gibbs energies of formation, standard enthalpies of formation, standard molar entropies, standard molar heat capacities, and standard transformed formation properties for the substances participating in this reaction. This reaction is used to manufacture L-tryptophan, which finds application as an antidepressant and is also one of the essential amino acids needed for growth. The enzyme L-tryptophanase is also used as an anti-tumor agent.

9. NMR Spectroscopy of Oligosaccharides Related to the O-Specific Polysaccharide of Shigella Dysenteriae Type 1

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P. Kovac (National Institute of Diabetes and Digestive and Kidney Diseases), and  
C.P.J. Glaudemans (NIDDK)

A series of oligosaccharide fragments of the capsular lipopolysaccharide of the Shigella dysenteriae type 1 bacterium has been synthesized, either by chain extension, or by block condensation. These oligosaccharides (comprised of three disaccharides, a trisaccharide, two tetrasaccharides, a pentasaccharide, and a hexasaccharide) are potential components of a future vaccine against Shigella dysenteriae type 1, which is a serious disease in the developing countries, and in children and immunocompromised patients. Nuclear magnetic resonance data measured by the selective 1D TOCSY, 2D TOCSY, and 2D COSY, HETCOR, HMQC, and HMBC techniques at proton resonance frequencies up to 600 MHz confirm the structures, anomeric configurations, and ring conformations of the oligosaccharides. The NMR data also indicate that the tetrasaccharide and the pentasaccharide partially mimic the conformation of the O-specific polysaccharide of the bacterium, whereas the hexasaccharide resembles this conformation more closely. In related work not reported here, these oligosaccharides are being used to study mechanisms of binding between the antigenic regions of the saccharides and murine, monoclonal antibodies raised against Shigella dysenteriae type 1.

10. Transport Phenomena in Biophysical Systems

J.B. Hubbard

A computational algorithm that yields very accurate estimates of the diffusive flux of energy, momentum, or mass toward or away from an object (molecule, aggregate, etc.) or a collection of objects having arbitrary shapes has been devised.

The translational friction coefficient and the capacitance (diffusion-limited reaction rate) of a variety of objects were calculated with a probabilistic method involving hitting the 'probed' objects with random walks launched from an enclosing sphere. This method was applied to exactly solvable examples and to physically important and analytically intractable examples (cube, chain of spheres at the vertices of self-avoiding and random walks, etc.) to test the program accuracy. Large fluctuations in the friction of polymer chains with a random coil structure gave rise to large deviations from the simple mean-field Kirkwood-Riseman theory, and the calculation of the rate constant of absorbing spheres randomly distributed on a spherical penetrable surface also showed a fluctuation induced enhancement relative to the mean-field estimate. Transients to the chemical rate constant and related properties were expressed in terms of fluctuations in the Wiener sausage (volume swept out by diffusing object), and the leading order transient depended on the diffusion coefficient, dimensionality  $d$ , and the square of the capacity.

11. 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 (Standard Reference Data Program),  
and J.E. Ladner

The crystal structure determination of biological macromolecules has been a critical tool in protein engineering and rational drug design, important areas of development in biotechnology. The complexity and variation in the surfaces of biological macromolecules relate to their solution properties and to how they will crystallize. Determination of the conditions which will induce crystallization is an empirical process often taking weeks or months of laboratory time. The NIST/NASA/CARB Biological Macromolecule Crystallization Database (BMCD) has been developed to assist in the design of strategies which hopefully can reduce the time it takes to discover crystallization conditions for a particular biological macromolecule. A new version of the database, Version 3.0 of the BMCD, includes crystal and crystallization data on all forms of biological macromolecules which have produced crystals suitable for x-ray diffraction studies through 1992 and is scheduled for release in early FY94. 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.

12. Spectroscopy of Nucleic Acid Radicals

M. Krauss and R. Osman (Mt. Sinai Medical Center)

Nucleic acid base radicals created by radiation damage initiate reactions that result in strand breakage. Optical spectroscopy is an important means of identifying these radical species. However, little is known of the electronic structure of these species and assignments of experimental spectra is difficult. Assignments of the spectra of tautomers formed by radical attack at different sites are important because of their very different redox properties and reactivity. The first ab initio calculations of the radical spectra of H and OH adducts of uracil

have been obtained. The calculated first absorption peak in the spectra of the H and OH adducts to the C5 and C6 positions in uracil are separated by nearly 200 nm. This result contradicts an experimental deduction that the C5H and C6H adduct spectra have similar peak positions and only differ in intensity. Other experimental assignments of uracil radicals have also been questioned. This preliminary work on the simplest base, uracil, suggests theoretical assignments can be used to identify these species and that experimental assignments for the other bases should be re-examined.

This work is part of an examination of radical spectroscopy in biomolecules in general. Preliminary work has been done on phenoxy and indolyl radicals that are models for Trp and Tyr side chain radicals.

13. Thermodynamics of Cyclic Nucleotide Binding to the Cyclic AMP Receptor Protein and Its Thr-127 -> Leu and Ser-128 -> Ala Mutants

F.P. Schwarz, J.L. Moore, K.H. McKenney, and S.T. Krueger (Reactor Radiation Division)

Activation of transcription regulation in procaryotes is initiated by the binding of cyclic Adenosine Monophosphate (cAMP) to the Cyclic AMP Receptor Protein (CRP). CRP is a homodimeric protein with one cAMP binding site per monomer subunit. The cAMP-CRP complex then binds specifically to DNA and activates transcription in the presence of RNA polymerase. The thermodynamics of the binding of cAMP and an homologue, cyclic Guanosine Monophosphate (cGMP), CRP and two mutants of CRP in 0.05 M potassium phosphate buffer (pH 7.0) + 0.2 to 0.5 M KCl have been investigated by titration calorimetry and by differential scanning calorimetry (DSC) at the denaturation temperature.

This information will be consolidated into a preliminary thermodynamic model of how CRP regulates gene expression in *E. coli*. This model will be important in understanding the activation and regulation of gene expression in a large number of living systems, thus, leading to improve strategies for the expression of genes and the engineering of novel proteins.

At 0.5 M KCl concentration, cGMP binds exothermically and independently to each site on CRP with a  $\Delta G^{\text{ob}} = -24.0 \pm 0.1 \text{ kJ mol}^{-1}$ ,  $\Delta H_b = -7.0 \pm 0.4 \text{ kJ mol}^{-1}$ , and  $\Delta S_b = 57 \pm 2 \text{ J mol}^{-1} \text{ K}^{-1}$  at 297.15 K. In contrast, the binding of cAMP to CRP is endothermic and cooperative at 297.15 K and is best described by a two-site interactive model. Using the equilibrium constant ( $K_b$ ) and enthalpy for cGMP binding to CRP as initial parameters for cAMP binding to form the CRP:cAMP complex, the two-site interactive model fit yields an enthalpy of  $48.1 \pm 2.1 \text{ kJ mol}^{-1}$  and a  $K_b = 1.4 \pm 0.1 \times 10^5 \text{ M}^{-1}$ . Measurements on cGMP and cAMP binding at 312.45 K yield a heat capacity change upon cGMP binding to CRP of  $300 \pm 15 \text{ J mol}^{-1} \text{ K}^{-1}$  and a heat capacity change of  $1.4 \pm 0.17 \text{ kJ mol}^{-1} \text{ K}^{-1}$  for cAMP binding to the complex CRP:cAMP. The binding thermodynamics are the same at 0.2 M KCl concentration.

The endothermic cooperative binding of cAMP to CRP suggests a conformational change occurs in CRP upon binding of cAMP, which is further substantiated by Small Angle Neutron Scattering (SANS) measurements. The radius of gyration from the SANS measurements is 2.92 nm for the uncomplexed CRP and 2.70 nm for the (cAMP)<sub>2</sub>-CRP complex, indicating that the volume of CRP is smaller in the complex. Further SANS measurements in H<sub>2</sub>O and on the CRP mutants are underway to determine the shape of CRP in solution.

The binding of the cyclic nucleotides to two CRP mutants consisting of Thr-127 substitution by leucine (T127L mutant) and a Ser-128 substitution by alanine (S128L mutant) is exothermic and entropically driven at 297.15 K and is best described by an independent two-site model. In contrast to CRP, binding of cGMP to the T127L mutant induces specific DNA binding and activates transcription. The binding isotherms of cGMP to the mutants yield thermodynamic parameters close to those of binding to CRP with the exception of the binding enthalpy to T127L which is  $-4.2 \pm 0.4$  kJ mol<sup>-1</sup> at 297.15 K. This increase in the binding enthalpy relative to that of cGMP binding to CRP suggests a partial conformational change of the T127L mutant upon cGMP binding. SANS measurements on T127L should substantiate this. Binding of cAMP to T127L is not observed calorimetrically, while binding of cAMP to S128A occurs with  $K_b = 2.0 \pm 0.4 \times 10^5$  M<sup>-1</sup> and  $\Delta H_b = -9.7 \pm 0.4$  kJ mol<sup>-1</sup>. Binding of cGMP or cAMP to S128A does not activate transcription.

Analysis of DSC measurements on the mutants yields one transition peak with calorimetric enthalpies and transition temperatures close to those of CRP. In the presence of cAMP and cGMP, the transition peaks do not exhibit the multiple transitions observed for CRP complexed with cAMP and cGMP. Apparently, the mutations also alter the domain interactions of the CRP complexed with cAMP and with cGMP.

#### 14. A Crystallographic Analysis of the Catalytic Mechanism and Substrate Specificity of Glutathione S-Transferase

G.L. Gilliland, X. Ji (CARB/UMD), and R.N. Armstrong (University of Maryland)

A number of X-ray crystal structure determinations of a rat liver mu class glutathione-S-transferase (GST) complexed with various ligands have been completed. An analysis of the results of glutathione S-transferase substrate, transition state analog, and product complexes is currently underway which is leading to a basic understanding of the structural role protein components play in determining substrate specificity and catalysis.

The three-dimensional structure of GST in complex with (9R,10R)- and (9S, 10S)-9-(S-glutathionyl)-10-hydroxy-9,10-dihydrophenanthrene, products of the addition of glutathione to phenanthrene 9,10-oxide, have been determined at 1.9 and 1.9 Å, respectively. These structures help to define the xenobiotic substrate binding site and implicated Tyr 115 in catalysis of this class of compound. Site directed mutagenesis studies confirmed this role for the tyrosine. This

residue is not important for catalysis involving other classes of substrates. This is one of the first structural studies which provide evidence for a variation in chemistry of catalysis for an enzyme depending upon which substrate is bound in the active site.

The three-dimensional structure of GST in complex with a transition state analogue, 1-(S-glutathionyl)-2,4,6-trinitrocyclohexadienyl, and product, 1-(S-glutathionyl)-2,4-dinitrobenzene, of a nucleophilic aromatic substitution reaction have been determined at 1.9 and 2.0 Å resolution, respectively. The two structures represent snap-shots along the reaction coordinate for the enzyme-catalyzed reaction of glutathione with 1-chloro-2,4-dinitrobenzene and reveal specific interactions between the enzyme, intermediate and product that are important in catalysis. The geometry of the intermediate and product have been used to postulate reaction coordinate motion during catalysis.

15. Protein Engineering Studies Directed Towards the Stabilization of a Calcium-Independent Form of Subtilisin BPN', a Detergent Additive

D.T. Gallagher, G.L. Gilliland, and P. Bryan (CARB/Univ. of MD)

Subtilisin BPN', a serine protease used in a variety of commercially available industrial and household detergents, continues to be the object of protein engineering studies at CARB directed at understanding the factors which affect protein folding and protein stability. A number of site-directed mutants of this protein have been characterized, crystallized and their structures determined using x-ray crystallographic procedures. The crystal structure analysis of a subtilisin BPN' variant in which the high-affinity calcium site was omitted was featured in *Proteins: Structure, Function and Genetics* (Vol. 16, pp. 205-213) in June of 1993.

This variant has reduced thermal stability compared to the natural enzyme, but the analysis suggests further modifications which may restore or even enhance the thermal stability. These protein engineering studies point the way to rational modification of proteins by introducing mutations to compensate for stability lost as a result of structural changes directed at altering the function of the macromolecule.

Subtilisin, because of its general utility as a detergent additive, has been chosen as the subject of an exhibit for "Science in American Life" a new Smithsonian exhibition scheduled to open in April of 1994. The Smithsonian display uses the x-ray structure of the protease and a substrate to produce a hands-on computer activity. The visitor attempts to correctly align the subtilisin molecule with the substrate so that catalysis can occur. This exhibit will introduce the visitor to the most up-to-date advances in molecular biology and computer graphics, and provide a sense of practical application of protein engineering.

## 16. Cobalt d-d Spectroscopy of Several Zinc Enzymes

M. Krauss and D.R. Garmer (Mt. Sinai Medical Center)

The visible spectroscopy of cobalt substituted zinc enzymes provides insight into the electronic and structural environment of the active site. Ab initio calculations of the d-d spectra of model complexes of cobalt are applied to an analysis of the following enzymes: liver alcohol dehydrogenase (LADH), carboxypeptidase A (CPA), thermolysin (TLN), and carbonic anhydrase (CA). For the well characterized active site of the LADH resting state, the calculated spectra agrees well with experiment both in the infra-red and visible. The spectra in the presence of metal bound deprotonated water or alcohol is predicted and can be used to characterize this stage of the reaction mechanism. Similarities in the active sites and resulting spectra of CPA and TLN are examined with models that explore the rotational flexibility of ligands implied by experimental differences in crystal and solution structures. Insight into the mechanism of anion inhibitor binding is obtained by comparing the spectra of CA with thiocyanate and cyanate. Experimental and theoretical spectra are in good agreement for thiocyanate but the theoretical cyanate spectra does not fit experiment. The spectra is found to resemble more closely the high pH form of the uninhibited CA which is in accord with the recent x-ray crystallographic observation that the cyanate binds in the second shell of the zinc active site. However, the present suggestion that the water bound to the cobalt is deprotonated leads to a different interpretation of the mechanism of binding of inhibitors like cyanate than proposed earlier. Although the cyanate in the second shell has a small effect on the d-d spectra of cobalt, the deprotonated water suggests that desolvated cyanate abstracts the proton from water.

## 17. Ab Initio Potential for Water Simulations

W.J. Stevens and D.R. Garmer (Mt. Sinai Medical School)

Modelling of condensed phase chemistry and dynamics is currently carried out with water-water interaction potentials that have been empirically adjusted to reproduce ambient properties such as pressure, heat capacity, and radial distribution functions. These empirical potentials do not include explicit many-body interactions, and hence cannot be used to study condensed-phase phenomena far from normal conditions. Specifically, the empirical potentials do not take into account electronic polarization. This deficiency is overcome through the use of fixed electrostatic potentials that deliberately exaggerate the dipole moment of the water monomer so that it more closely resembles the solution-phase average (2.5 Debye) rather than the gas phase value (1.85 Debye). The exaggerated dipole moment is usually represented by fixed point charges located on the atoms of the water molecule and perhaps one other point such as the molecular center of mass. This electrostatic representation exhibits a strong directionality that mimics the behavior of water at normal temperatures and pressures. However, at high temperatures or low pressures, where water is more freely rotating, the average dipole moment should be more like the gas-phase monomer value, since the electronic polarizability of water is nearly isotropic. Recently,

we have developed an *ab initio* potential based on quantum mechanical calculations of the molecular properties of water and the interactions of water dimers that will be useful for modelling water under all conditions. The potential contains explicit electronic polarization terms. Large-scale calculations were used to obtain accurate water wavefunctions that reproduce the gas phase electronic properties such as the electrostatic potential and the polarizability. The electrostatic potential was fit with a spatially distributed multipolar expansion, and the polarizability was decomposed into spatially distributed bond and lone pair electronic contributions. Several hundred calculations were carried out on the water dimer, to map out the potential energy surface. At each point, the classical electrostatic and polarization interactions of the two monomers were subtracted from the *ab initio* dimer interaction energy. The residual interaction term represents the non-classical exchange/orthogonality interaction that gives rise to the repulsive wall on the potential energy surface. This energy component was fit with a sum of atom-atom exponential repulsions, with the parameters adjusted to reproduce the *ab initio* interaction energies. The result is a new two-body potential that incorporates many-body effects through polarization. Thus, the water monomer dipole moment in this new model is equal to the experimental gas-phase value, rather than the much larger value used in the empirical potentials that do not include polarization. This will have an impact in molecular dynamic modelling under conditions where the empirical potentials exhibit an exaggerated directionality due to the large fixed monomer dipole.

18. Thermodynamics of Hydrogen Cyanide and Hydrogen Fluoride Binding to Cytochrome c Peroxidase and Its Asn-82 -> Asp Mutant

F.P. Schwarz, S.F. DeLauder (Chemistry Department, Howard University), J.M. Mauro, T.L. Poulos (CARB/UMBI), and J.C. Williams (Chemistry Department, Howard University)

The ferric heme of yeast cytochrome *c* peroxidase (CCP) [EC1.11.1.5] reacts rapidly (rate constant  $\geq 10^7 \text{ M}^{-1}\text{s}^{-1}$ ) and efficiently with hydrogen peroxide to yield a 2 electron oxidized enzyme intermediate commonly termed Compound I:



The reaction cycle is completed through reduction of Compound I by reducing equivalents supplied by ferrous cytochrome *c*. The geometry of the peroxide binding and cleavage site is clearly optimized for essentially irreversible heterolytic O-O cleavage; however, in common with other ferric heme proteins, a number of other small ligands bind, but reversibly, to the ferric iron.

CCP is the most thoroughly studied electron transfer enzyme and its structure has been determined at high resolution by X-ray crystallography. An understanding of the electron transfer



mechanism can facilitate the design and engineering of proteins with novel electron transfer properties such as those used as photocells or biochips.

Studies of the thermodynamics of the reversible binding of small ligands such as fluoride and cyanide should yield some understanding of the structural factors in the CCP active site which contribute to efficient peroxide binding.

The thermodynamics of fluoride and cyanide binding to cytochrome  $c$  peroxidase (CCP) and its Asn-82- > Asp Mutant (D82CCP) in phosphate and acetate buffer at ionic strength of 0.15 from pH 5.0 to 7.1 were investigated by titration calorimetry at 289 and 297 K. The binding reactions are essentially enthalpically driven. The fluoride binding constants determined from the titration calorimetry results were in agreement with the binding constants determined from difference spectroscopy measurements. For cyanide binding to CCP at 297.9 K, the binding constant decreased from  $8.95 \pm 0.83 \times 10^5 \text{ M}^{-1}$  at pH 7.0 to  $4.04 \pm 0.23 \times 10^5 \text{ M}^{-1}$  at pH 5.0 and the binding enthalpy increased from  $-57.2 \pm 1.4 \text{ kJ mol}^{-1}$  at pH 7.0 to  $-48.6 \pm 1.8 \text{ kJ mol}^{-1}$  at pH 5.0. For fluoride binding to CCP, the binding constant increased from  $8.41 \pm 0.54 \times 10^3 \text{ M}^{-1}$  at pH 7.0 to  $3.11 \pm 0.09 \times 10^5 \text{ M}^{-1}$  at pH 5.0 and the binding enthalpy increased from  $-71.9 \pm 1.1 \text{ kJ mol}^{-1}$  at pH 7.0 to  $-67.0 \pm 1.9 \text{ kJ mol}^{-1}$  at pH 5.0. The binding enthalpies for D82CCP were about the same as those for CCP. However, the cyanide and fluoride binding constants to D82CCP were, respectively, a factor of two less and at least an order of magnitude less than the corresponding binding constants of CCP. Decreased ligand binding strength in the D82CCP mutant is, thus, entirely due to entropic effects.

## 19. Mechanism of Ligand Induced Gene Activation

K.H. McKenney, J.L. Moore, J. Zondlo (CARB/UMBI), and F.P. Schwarz

Protein-ligand interactions are responsible for regulating many biological processes essential for growth, viability and signal transduction. Protein binding of ligands frequently produces a conformational change in the protein which can significantly alter the protein's function and activity. The cyclic AMP receptor protein (CRP) of *E. coli* and its small molecule ligand, cAMP provide an important model system for studying the protein-ligand interaction required for regulation of gene expression in a large number of living systems. Using the model of the three dimensional structure of CRP with bound cAMP determined by x-ray crystallographic methods, in conjunction with molecular genetic, molecular biological, biochemical, and biophysical methods and techniques, specific chemical side chain substitutions have been made in CRP via codon changes in the gene coding for CRP to define the role and function of specific chemical contacts essential for CRP function. Six pairs of amino acid side chains important for protein-ligand function in the CRP dimer have been discovered. Four pairs of amino acids function as "anchor" contacts, important for recognition of the sugar and cyclic phosphate moieties of cAMP, while the other two amino acid pairs function as "specificity" contacts to recognize the purine ring of cAMP. With this information, in conjunction with previous work,

a model has been developed for ligand induced conformation change that results in signal transduction and gene activation. This model for ligand induced conformational change is being tested by rigorous characterization of the ligand site mutants using a number of genetic, biochemical and biophysical techniques and methods, including in vivo transcriptional activation and repression assays, in vitro DNA binding and bending assays, analytical ultracentrifugation, titration and scanning calorimetry, circular dichroism, low angle neutron diffraction, and solution NMR.

## 20. Regulation of the Escherichia coli Adenylyl Cyclase Activity by Protein IIA<sup>Glc</sup> of the Phosphoenolpyruvate: Glucose Phosphotransferase System

P.T. Reddy

Modulation of the activity of regulatory enzymes by protein-protein interactions is a phenomenon essential for biological regulatory processes. The regulatory enzyme adenylyl cyclase (formerly called adenylate cyclase) is of particular importance for the cell because this enzyme synthesizes a second messenger molecule, cyclic adenosine monophosphate (cAMP). cAMP has been shown to modulate gene expression and play a role in the transformation of bacterial cells by plasmid DNA. It is therefore essential to understand how cAMP concentration in the cell is stringently regulated by the modulation of adenylyl cyclase activity.

Experimental evidence suggests a role for Protein IIA<sup>Glc</sup> of the phosphoenolpyruvate: glucose phosphotransferase system (PTS) protein(s) in the regulation of adenylyl cyclase activity and consequently cAMP levels in the cell. To assess the role of phosphorylation of Protein IIA<sup>Glc</sup> in the regulation of adenylyl cyclase activity, both the catalytic histidine (His 90) codon and the regulatory histidine (His 75) codon were each mutated to code for glutamate and glutamine. Adenylyl cyclase assays were performed in a *crr* (the gene that codes for Protein IIA<sup>Glc</sup>) deletion strain of *E. coli* transformed with a plasmid carrying the wild type *crr* gene as well as all the four mutant forms. Wild type IIA<sup>Glc</sup> and [Gln<sup>75</sup>] IIA<sup>Glc</sup> are equally potent activators (4 fold) of adenylyl cyclase. [Glu<sup>75</sup>] IIA<sup>Glc</sup> enhanced the activity to a lesser extent (2 fold) while [Gln<sup>90</sup>] IIA<sup>Glc</sup> and [Glu<sup>90</sup>] IIA<sup>Glc</sup> did not. The level of stimulation of adenylyl cyclase activity by IIA<sup>Glc</sup> and its mutants correlates with the phosphorylation of  $\alpha$ -methylglucoside. Taken together, these results suggest that phospho Protein IIA<sup>Glc</sup> is an activator of adenylyl cyclase.

## 21. Nonspecific Protein Binding

R.W. Ashton

Biosensors that measure protein-protein and enzyme-substrate interactions rapidly and inexpensively have important biotechnological and biomedical applications. A problem with the application of the technology is the non-specific binding (NSB) interaction of proteins with sensor

surfaces. This interaction contributes to the measured signal, increasing the signal-to-noise ratio of the measurement.

The goal of this research, which is sponsored by the Consortium on Advanced Biosensors, is to find ways of minimizing NSB. However, it is first necessary to gain an understanding of the mechanism(s) involved in NSB. To do this we will systematically examine the interactions of proteins with highly defined surfaces. We can create highly defined surfaces of various types by using alkylthiols  $[SH(CH_2)_nR]$  to form self-assembled monolayers (SAMs) on gold films. The nature of the surface depends on the surface exposed R group with which the alkylthiol is functionalized. For example, it is possible to create surfaces with  $-CH_3$ ,  $-OH$ ,  $-COOH$ ,  $-SH$ ,  $-SO_4$ , or more complex groups, such as carbohydrate polymers, as the exposed group. Adsorption will be studied under conditions of varying pH and ionic strength.

The SAM surfaces will be characterized by contact angle goniometry, electrochemistry and ellipsometry. Protein adsorption to the SAM surfaces will be studied using radioisotopically labelled proteins, ellipsometry, surface plasmon resonance (SPR) and surface enhanced raman spectroscopy (SERS). The last two types of experiments will be carried out in collaboration with the Biophysical Measurements group.

The well characterized proteins bovine serum albumin (BSA) and human immunoglobulin (hIgG) will be used in these experiments. Because of the available structural information for these proteins it should be possible to correlate protein structure with the measured binding interactions. The information gained from these studies will be used in an attempt to construct a model for the NSB mechanism. Such a model would be used as a guide as we explore ways of minimizing NSB.

## 22. Light and Potential Addressable Immunosensors

**S.A. Glazier**

The goal of this work is the construction of immunosensors which can screen for the presence of analyte antigens and haptens. These sensors employ novel addressing systems which allow multiple analytes to be detected by a single device. In the case of light addressable sensors, novel 9,10-anthraquinone sulfonyl chlorides are being studied as light activated, hydrogen peroxide producing labels for use in the immunoassays which will be conducted by the sensors. The light addressability allows several assays to be performed on a single sample simultaneously with the detection of each immunoassay occurring sequentially by measurement of hydrogen peroxide production.

In the case of the potential addressable sensors, the design of the sensors is similar to those above, except they will employ ruthenium (II) bipyridyl labels. These labels, commercially available in early 1994, exhibit electrogenerated chemiluminescence (ECL) under suitable solution

conditions. Using these sensors, several assays will be performed simultaneously on a single sample with the detection of each immunoassay occurring sequentially by measurement of ECL production.

This project is in its infancy, but promises to yield sensors which are generic, sensitive, and able to screen for multiple sample components.

### **23. Characterization of Staphylococcus Alpha-Toxin Self-Assembled Pores in Black Lipid Membranes**

**J.J. Kasianowicz and B. Robertson**

A numerical description of the effect of pH, salt concentration, and membrane potential on the current through a channel protein in a phospholipid bilayer membrane has been developed, in good agreement with experiment.

Experimental work has been done on the current-voltage relation of alpha-toxin, which self-assembles into phospholipid bilayer membranes. Six alpha-toxin molecules spontaneously imbed themselves in the membrane and form a 2 nm-diameter pore through the membrane. When a voltage is applied across the membrane, electric current is carried through the pore by the salt ions that are in the aqueous solution in the pore and on either side of the membrane. Depending on pH and salt concentration, the ion flux through the pore is of much larger magnitude for a positive membrane voltage than for a negative one of the same magnitude. Thus the pores behave like rectifiers.

At first glance, this is difficult to understand. How can a (roughly circular) cylindrical hole that is 5 nm long and 2 nm in diameter pass ions through the membrane more readily in one direction than in the other? The pore is certainly big enough that hydrated salt ions can get through without steric interference; the salt ions are not expected to bind to the protein; and the protein does not undergo a conformational change.

The answer is that fixed electric charges on certain alpha-toxin residues attract ions of the opposite sign from the solution. For example, assume that there are fixed negative ions on the left and fixed positive ions on the right. These attract an excess of positive ions in the solution on the left and an excess of negative ions on the right. If the applied voltage tends to move positive ions in the solution from left to right and hence negative ions from right to left, then the high-concentration ions move into the pore, and a large current flows through the pore. If the opposite voltage is applied, the high-concentration ions move away from the pore, and a much smaller current flows through the pore. Since the current through the pore must be identical to the measured electric current, this explains the rectifying effect.

This effect is reduced at low pH because protons from solution bind to histidines in the protein and screen the fixed charge with a pK near 6 as expected. The model involves solving the continuity equations for positive and negative ions that diffuse and migrate in the electric field. These are coupled to an equation relating potential and charge. The charge on the histidines is described by chemical thermodynamics. The calculated result agrees with experiment within a few percent.

The understanding obtained will aid the rational design of membrane channel mutants suitable for molecular electronics.

## **24. Electro-Optical Properties of Bacteriorhodopsin in Black Lipid Membranes**

### **B. Robertson and J.J. Kasianowicz**

This project has been initiated to better understand the mechanism of the bacteriorhodopsin photocycle. The present model explaining the photocycle sequence has been developed, based upon studies carried out at low temperatures designed to slow the lifetimes of the several intermediate states. The model still does not fit the available data. We believe this approach will allow improvement of the photocycle model by developing new data on the photocycle intermediation.

These experiments involve reconstituting bacteriorhodopsin into lipid membranes, applying pulsating light, and measuring the effect of the light on the protein. The literature on the kinetics of bacteriorhodopsin (BR) has been reviewed. An apparatus for forming the lipid membrane—a vibration-free and electromagnetically-shielded environment—has been designed, constructed, and used with a detector.

As a model, a lipid membrane was formed on a 250 micron hole using diphylanoyl phospholipidylcholine, a phospholipid, selected because of its stability. The resolution of the hydrogen ion movement through its lipid membrane was measured and found to be 2000 protons per second. Since bacteriorhodopsin cycles in 10 milliseconds, and since with synchronous detection the light is off half of the time, the measurement indicates that the minimum detectable number of BR molecules in the membrane would be forty.

The light intensity obtained with the fiber-optic light system used for viewing the membrane was found to be way too small to produce a detectable effect on bacteriorhodopsin. An arc lamp and a system of heat filters and lenses for focussing light directly onto the membrane has been designed, and assembled.

Initial studies with bacteriorhodopsin in the membranes have so far been unsuccessful because the lipid membrane breaks within a matter of seconds. Modification of the lipid materials are planned to improve membrane stability.

**25. Characterization of Bacteriorhodopsin Modified Gelatin Films for Sensitivity and Resolution**

**H.H. Weetall, N.N. Vsevolodov (USSR Academy of Science, Institute of Biological Physics, Moscow, Russia), and T.V. Dyukova (USSR Academy of Science, Institute of Theoretical and Experimental Biophysics, Moscow, Russia)**

The object of the research was to immobilize bacteriorhodopsin (BR) molecules in air-dried gelatin films and investigate the changes in the photochemical transformations in BR as the chemical environment of BR molecules is varied. The life-time of the M state, the key intermediate of the BR photocycle, strongly depends on the dehydration state, pH, temperature and the chemical environment of BR molecules. Several combinations of chemical additives increasing M decay time were developed. The additives were also shown to increase 2 to 3 times the maximum bleaching of the BR film at 570 nm.

The comparative photoinduced spectral and kinetic characteristics of purple membranes solubilized with two non-ionic detergents Triton X-100 and Octyl- $\beta$ -d-glucoside and embedded in gelatin films were studied. A blue shift for the maxima of the ground and photoinduced states was observed in both detergents. In Triton X-100 it was more pronounced. Electron micrographs showed the formation of micellar structures of monomeric BR as the detergent concentration increased.

The formation and the decay times were measured at different detergent concentrations. The formation time of the M state was independent of the detergent type, concentration and light intensity. However, the total life-time of the M state increased at greater detergent concentrations. The BR-detergent interaction slowed down the M-to-ground state transition of the photocycle resulting in the M-state accumulation, which, in turn, caused increased photosensitivity of the solubilized samples as compared to the control. Photosensitivity is defined here as the ratio of a photoinduced absorbance change of the ground state related to the quantity of the photoactive molecules. For Triton-treated samples the photosensitivity was much higher as compared with that of the Octyl-glucoside-treated samples. We have explained the results by the formation of tubular structures first, and then micelles, resulting in the change of the BR tertiary structure and disturbance of the normal course of the structural relaxation process.

The holographic sensitivity of the BR films vs. solubilization extent was also studied. The diffraction rise and decay kinetics of the BR films at varying detergent concentration were taken. An increase in the diffraction efficiency of the films was observed at greater detergent concentration. Thus, purple membrane solubilization seems to be a promising tool to optimize the parameters of the BR films.

## 26. Light Activated Enzyme Switch for Use in a Biosensor

M.F. McCurley and S.A. Glazier

The active element of many biosensors is an enzyme. Methods for controlling the activity of the enzyme in biosensors include enzyme cascades and metabolically controlled switches whose activation is dependant on the concentration of a particular metabolite, e.g., glycogen phosphorylase B activation in the presence of AMP. A method for optically controlling the activity of enzymes is being developed in this laboratory. The principle of the switch under investigation is to control the enzyme activity by controlling the pH in the microenvironment of the enzyme. The activity of many enzymes are known to respond to a change in solution pH. The trigger for the switch is bacteriorhodopsin (BR), a membrane protein, which pumps protons when it is irradiated with light of a particular wavelength. The bacteriorhodopsin is oriented so that protons are pumped preferentially in one direction by immobilizing it in phosphatidylcholine vesicles. Protons are pumped into the BR-vesicle when the complex is irradiated with 570 nm wavelength light. The pH of the exterior solution becomes more basic and the interior becomes more acidic. The change in pH of the solution due to pumping by the bacteriorhodopsin-vesicle complex was found to be 0.3 pH units. pH activity curves of BR-vesicle bound enzymes are being investigated. The change in the activity of the enzyme bound to the bacteriorhodopsin-vesicle complex following illumination is also under study.

## 27. Intercalation of Carcinogens and Other Toxic Molecules into DNA

J.J. Horvath and D. Penumatchu (University of Madras, Madras, India)

The detection of carcinogens in air is a time consuming process whereby air is pushed through a urethane filter for 12-24 hours, extracted and then detected using GC or GC-MS. This process is expensive particularly since many negative samples are processed along with the positive samples. What is needed is simple, rapid, and sensitive general assay methodology for carcinogens, which can eliminate the negative samples before further processing.

Since there are a large number of intercalating areas in a typical DNA molecule, it is possible to obtain a very large signal for a small quantity of DNA. It is also well known that many carcinogenic molecules are DNA intercalating agents. Since both the dye and the carcinogen intercalate into DNA it is possible to set up a competitive binding reaction, similar to an antigen/antibody reaction, whereby the amount of intercalating dye bound is inversely proportional to the amount of carcinogen bound.

Two methods of detecting the carcinogens in DNA competitive binding reactions are being examined. The first method involves fluorescent polarization spectroscopy. A fluorescent dye molecule, when free in solution, will exhibit little fluorescence polarization since the molecules rotate freely and quickly. A DNA intercalated dye molecule will show strong polarization

because its movement is limited by the binding, and the DNA, being large, will rotate very slowly in comparison to the free dye. The first carcinogens investigated were benzo(a)pyrene, benzidine, aniline, parathion, pentachlorophenol and nitrobenzene as test compounds. Of these molecules, only benzo(a)pyrene showed a positive response with a detection limit of 5.7 parts per billion (ppb).

Further studies indicated that positive intercalators required at least two fused benzene rings, while molecules containing two connected benzene rings like benzidine do not intercalate. The effects of chemical side groups was examined using a series of 8 anthraquinone derivatives. Current polarization studies are centered on relating carcinogenicity to DNA intercalation strength for a possible alternative to the Ames test, using classified polycyclic aromatic hydrocarbons with differing degrees of carcinogenicity ranging from class 1 (not carcinogenic) to class 6 (strongly carcinogenic).

The second method of detection uses evanescent wave technology. DNA is bound to the sides of an optical wave guide. The intercalation reaction is monitored in real-time by measurement of the evanescent wave. This method should yield a very sensitive, rapid, and potentially portable technique for detection of carcinogens. The recent work in the evanescent wave fiber optic program has been to find a way to bind DNA to the optical fibers. A technique was developed using single-stranded DNA, treated with  $\text{NaIO}_4$  which is then coupled to the fused silica fiber after its treatment with 3-Aminopropyltriethoxysilane. After reaction, the remaining single-stranded DNA is added and kept overnight at  $37^\circ\text{C}$  for recombination into double-stranded DNA. This technique has shown promise for future work.

## 28. Characterization of Phospholipid/Alkanethiol Bilayer Membranes on Planar Surfaces

### A.L. Plant

Lipid bilayer membranes form the natural boundaries of cells and behave as selective barriers to extracellular molecules. Their primary component is phospholipid molecules, but the cell membrane also provides a matrix for proteins with receptor and transport functions. In addition to keeping the inside and the outside of the cell apart, the cell membrane, through its lipid and protein components, also allows regulated communication between the two compartments. Models of cell membranes provide a way of studying the mechanisms of specific biochemically-regulated signal transduction between two chemically and electrically isolated compartments. These mechanisms and materials may have relevance to biosensors.

Few models of phospholipid bilayers are rugged enough to be considered useful in sensor applications. Model bilayer membranes which are composed of a monolayer of alkanethiols covered by a monolayer of phospholipid molecules are being studied. Alkanethiols interact strongly with metals such as gold, and spontaneously form reproducible and rugged monolayers on gold electrodes. The interaction of the hydrophobic portion of phospholipids with the



hydrophobic alkanethiols is also a spontaneous process driven by highly favorable thermodynamics. The result of this two-step self-assembly process is an electrode coated with a rugged bilayer which closely resembles a phospholipid membrane.

These layers have been characterized primarily by their electrical characteristics such as capacitance and resistance. The bilayers are highly impermeable to ions. However, in the presence of melittin, the peptide toxin of bee venom, the permeability of these bilayers increases dramatically. Melittin interacts with natural membranes as small monomers, and then self-assembles within the bilayer to form a pore through which ions can diffuse. The response of phospholipid/alkanethiol bilayers to melittin is analogous to that of natural cell membranes. Other studies which confirm the similarity between these bilayers and natural lipid membranes are the effect of phospholipid acyl chain length on the apparent thickness of the layer, and the effect of temperature on the membrane microstructure. Thus, it is anticipated that this model system will allow the study of the effect of protein receptor recognition at the membrane interface. Such multivalent interactions can drive the spontaneous organization of microdomains in membranes. At the level of the cell, these nanostructures can result in signal transduction through an otherwise insulating membrane. Mimicking this phenomenon may allow us to chemically couple biomolecular recognition events with electron transfer.

## 29. Immobilization and Characterization of Bacteriorhodopsin in Sol-Gel Glasses

H.H. Weetall

The light-sensitive protein, bacteriorhodopsin (BR) isolated from the bacteria Halobacterium halobrium has been immobilized in a sol-gel glass. For these studies, the immobilized D96N mutant form of the protein was used. This mutant form, unlike the wildtype protein, has an Arg at the Asp96 position in the peptide chain. The loss of this carboxylated amino acid residue destroys the ability of the molecule to correctly pump protons across the cell membrane. The resulting BR has a photocycle slowed considerably and totally dependent of the environmental pH.

Characterization of the immobilized D96N mutant has shown, as expected, that the photocycle half-times are pH dependent, with the slowest times occurring at alkaline pH values. In addition, the bleaching efficiency (the ability of the molecule to shift maximum wavelength in the presence of light) is also pH dependent. However, unexpectedly, the addition of guanidine, a compound which decreases the half-time of the wildtype photocycle, does the opposite for the mutant. Addition of guanidine causes the molecule to resemble the wildtype protein by greatly increasing the photocycle times and decreasing the bleaching efficiency.

The applications of BR include: gating, holography, memory storage, and imaging. Because of the photovoltaic properties, the molecule also has application as an artificial retina. Our studies are directed toward control of the photocycle so that we can stop the cycle as we choose

and thus store a byte of information in each molecule or pixel. Upon either electrical or optical stimulation, the photocycle would go to completion thereby allowing us to read and clear the device.

**C. Outputs and Interactions  
(Biotechnology Division)**

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- Tewari, Y.B. and Goldberg, R.N., "An Equilibrium and Calorimetric Investigation of the Hydrolysis of L-Tryptophan to (Indole + Pyruvate + Ammonia)," *Journal of Solution Chemistry* (in press).



- Weetall, H.H., "Preparation of Immobilized Protons," *Appl. Biochem. Biotech.* 41, 157 (1993).
- Weetall, H.H., Robertson, B., Cullin, D., Brown, G., and Walch, M., "Bacteriorhodopsin Immobilized in Sol-Gel Glass," *Biochim. Biophys. Acta* 1142, 211-213 (1993).
- Weetall, H.H., "The Activation of Inorganic Carriers by Silanization," *Biosensors and Bioelectronics* 8, No. 5 (1993).
- Wickner, S., Skowrya, D., Hoskins, J., and McKenney, K., "DnaJ, DnaK and GrpE Heat Shock Proteins are Required in oriP1 DNA Replication Solely at the RepA Monomerization Step," *Proc. Natl. Acad. Sci. USA.* 89, 10345-10349 (1992).

## 2. Talks

- Abramowitz, S., "Thermodynamic Properties of Species of Importance to Ozone Depletion," International Conference on Thermodynamics of Solutions and Biological Systems, New Delhi, India, January 5, 1993. Invited
- Atha, D.H., "Thermodynamic Analysis of Heparin Binding to Human Antithrombin," NIH Interinstitute Conference on Glycobiology, Bethesda, MD, January 12, 1993.
- Atha, D.H., "Physiochemical Characterization of Heparin," CHI Conference on Glycotechnology, San Francisco, CA, May 17, 1993.
- Atha, D.H., "Physiochemical Characterization of Low Molecular Weight Heparin," The 4th International IBC Symposium on Anticoagulants and Antithrombotics, Boston, MA, September 17, 1993.
- Cabezas, H., "A Review of the Theory of Phase Formation and Solute Partitioning in Aqueous Two-Phase Systems," 8th International Conference on Partitioning in Aqueous Two-Phase Systems, Leipzig, Germany, August 25, 1993. Invited
- Cole, K.D., "Electrophoresis and Electrochromatography in an Improved Vertical Column," 205th American Chemical Society Meeting, Denver, CO, March 29, 1993.
- Cole, K.D., "On the Use of Electrochromatography for Preparative Protein Purification," *Frontiers in Bioprocessing III*, Boulder, CO, September 22, 1993.
- Collison, M.E., Tarlov, M.J., and Plant, A.L., "Design of Biosensor Interfaces Using Molecular Self-Assembly Phenomena," American Chemical Society National Meeting, Chicago, IL, August 26, 1993.

- Coxon, B., Pozsgay, V., Glaudemans, Yeh, H., Robbins, J.B., and Schneerson, R., "Nuclear Magnetic Resonance Spectroscopy of Oligosaccharides Related to the O-Polysaccharide of Shigella Dysenteriae Type 1," Washington Area NMR Group, National Institutes of Health, Bethesda, MD, April 30, 1993.
- Coxon, B., Pozsgay, V., Kovac, P., Glaudemans, C.P., Robbins, J.B., and Schneerson, R., "Studies of Oligosaccharides That Can Recognize a Monoclonal Anti-Shigella Dysenteriae Type 1 Antibody," Fourth European Symposium on Organic Reactivity: Physical and Biological Aspects, Newcastle Upon Tyne, England, July 13, 1993.
- Coxon, B., Poszgay, V., Glaudemans, C.P.J., Robbins, J.B., and Schneerson, R., "Nuclear Magnetic Resonance Spectroscopy of Oligosaccharides Than Can Recognize a Monoclonal Anti-Shigella Dysenteriae Type 1 Antibody," 206th American Chemical Society Meeting, Chicago, IL, August 24, 1993. Invited
- Dizdaroglu, M.M., "Oxidative DNA Damage and Its Measurement," Mechanisms of DNA Repair, Oxidative Damage, Oslo, Norway, June 24, 1993. Invited
- Dizdaroglu, M.M., "DNA Damage by Oxygen Derived Species," American Chemical Society Middle Atlantic Regional Meeting, Long Island, NY, June 4, 1993. Invited
- Dizdaroglu, M.M., "Metal-ion Mediated Oxidative DNA Damage in Mammalian Chromatin In Vitro and In Vivo," Second International Meeting on Molecular Mechanisms of Metal Toxicity and Carcinogenicity, Madonna di Campiglio, Italy, January 11, 1993. Invited
- Dizdaroglu, M.M., "Oxidative DNA Damage in Mammalian Chromatin," Washington Chromatography Discussion Group, Rockville, MD, November 19, 1992. Invited
- Edwards, J.J., "Supercritical Fluid Extraction of Phospholipids," American Chemical Society, Division of Environmental Chemistry, Denver, CO, March 28, 1993.
- Gaigalas, A.K., "Momentum and Transport in Concentrated Protein Solutions," American Institute of Chemical Engineers 1992 Annual Meeting, Miami, FL, November 4, 1992.
- Gaigalas, A.K., "Mesh Size Pore Measurement in Rigid and Flexible Polyelectrolyte Matrices," (Poster), Symposium on Polyelectrolytes, Denver, CO, April 1, 1993.
- Gaigalas, A.K., "Application of SERS to the Study of Biomolecules on Electrode Surfaces," Joint Meeting of the Society for Industrial Microbiology and the Canadian Society for Microbiologists, Toronto, Canada, August 3, 1993. Invited
- Glazier, S.A., "Fluorescence Measurement of Tetracycline in Natural Media," 205th National American Chemical Society Meeting, Denver, CO, March 30, 1993.

- Gilliland, G.L., "The 2.2 Å Three Dimensional Structure of Glutathione S-Transferase from the MU Gene Class," The George Washington University, Washington, DC, October 27, 1992. Invited
- Gilliland, G.L., "Crystallographic Studies of the Mechanism and Substrate Specificity of Class MU Glutathione S-Transferase," Fifth Annual Siemens Area Detector User Group Meeting, Braunschweig, Germany, April 29, 1993. Invited
- Gilliland, G.L., "The Biological Macromolecule Crystallization Database and NASA Protein Crystal Growth Archive," Protein Crystal Growth in Microgravity Conference, Panama City Beach, FL, April 26, 1993. Invited
- Gilliland, G.L., "Crystallographic Studies of Glutathione S-Transferase a Detoxification Enzyme," Life Technologies, Inc., Rockville, MD, May 5, 1993. Invited
- Gilliland, G.L., "Crystallographic Studies of the Catalytic Reaction of Glutathione S-Transferase," Dept. of Biochemistry, Univ. of Rome, Rome, Italy, May 14, 1993. Invited
- Gilliland, G.L., "The Biological Macromolecule Crystallization Database, Version 3.0: New Features, Data, and the NASA Archive for Protein Crystal Growth Data," Fifth International Conference on Crystallization of Biological Macromolecules, San Diego, CA, August 11, 1993. Invited
- Gilliland, G.L., "The Active Site of Ribonuclease A: An Example of Solvent Modulated Specificity," Third International Meeting on Ribonuclease, Chemistry, Biology, and Biotechnology, Capri, Italy, May 10, 1993. Invited
- Goldberg, R.N., "Microcalorimetry," Inorganic Analytical Research Division, National Institute of Standards and Technology, Gaithersburg, MD, November 3, 1992. Invited
- Goldberg, R.N., "Thermodynamics of Enzyme-Catalyzed Reactions: Oxidoreductases," International Conference on Thermodynamics of Solutions and Biological Systems, New Delhi, India, January 4, 1993. Invited
- Goldberg, R.N., "Thermodynamics of Biochemical Reactions: Equilibrium and Calorimetric Measurements," Indian Institute of Technology, New Delhi, India, January 8, 1993. Invited
- Goldberg, R.N., "Thermodynamics of Biochemical Reactions," Indian Institute of Technology, Bombay, India, January 13, 1993. Invited

- Goldberg, R.N., "Thermodynamics and Bioprocess Optimization", National Renewable Energy Laboratory, Golden, Colorado, July 16, 1993. Invited
- Hancock, D.K., "Solution Structure and IgG Binding Site of the Streptococcal Protein G B2 Domain," Frontiers of NMR in Molecular Biology III, Taos, NM, March 13, 1993.
- Horvath, J.J., "Detection of Carcinogens by DNA Intercalation," 31st Annual Eastern Analytical Symposium and Exposition, Somerset, NJ, November 16, 1992. Invited
- Horvath, J.J., "Intercalative DNA Binding of Carcinogens and Their Detection," American Chemical Society's 27th Annual Middle Atlantic Regional Meeting, Hempstead, NY, June 3, 1993.
- Kasianowicz, J.J., "Genetically Engineered Pores for New Materials," Materials Research Society Meeting, Boston, MA, November 30, 1993.
- Kasianowicz, J.J., "Current Fluctuations Reveal Protonation Dynamics and Number of Ionizable Residues in the Alpha-Toxin Channel," Biophysical Society Meeting, Washington, DC, February 18, 1993.
- Kasianowicz, J.J., "Protonation Dynamics in a Channel," 11th International Biophysics Congress, Budapest, Hungary, July 27, 1993, (Poster). Invited
- Kasianowicz, J.J., "Ionic Current Noise Analysis as a Structural Probe of the Staphylococcus Aureus Alpha-Hemolysin", 2nd International Conference on Pore-Forming Toxins, Mainz, Germany, September 30, 1993. Invited
- Kline, M.C., "A Comparison of Methods for Electrophoretic Separations of Short Repeat Tandems," Fourth International Symposium on Human Identification, Scottsdale, AZ, September 27, 1993.
- Kline, M.C., "DNA Collections on Bloodstain Cards and Buccal Swabs," Annual Meeting of the American Academy of Forensic Sciences, Boston, MA, February 18, 1993.
- Krauss, M., "Spectral Shifts in Indole Fluorescence," Conference on Chemical Defense Research-US Army, Aberdeen Proving Ground, MD, November 20, 1992.
- Krauss, M., "Electronic Spectroscopy and the Reaction Field," Third World Congress of Theoretical Organic Chemists, Toyohashi, Japan, July 18-24, 1993. Invited
- McCurley, M.F., "Coupling Polymer Swelling to a Change in Fluorescence Intensity for a New Fiber Optic Sensing Technique," The Electrochemical Society, Honolulu, HI, May 17, 1993.

- McKenney, K.H., "Role of Heat Shock Proteins in Regulating Protein Function and DNA Replication," Life Technologies Inc., Rockville, MD, June 3, 1993.
- McKenney, K.H., "Tools of Molecular Engineering," The George Washington University School of Medicine, Department of Biochemistry and Molecular Biology, Washington, DC, February 9, 1993.
- McKenney, K.H., "Elucidating the Molecular Function and Mechanism of Stress Protein Action in Replicating DNA," University of Maryland Biotechnology Symposium, Rockville, MD, January 13, 1993.
- McKenney, K.H., "Role and Function of Heat Shock Proteins in DNA Replication," The George Washington University, Department of Genetics, October 13, 1992.
- Plant, A.L. and Tarlov, M., "Self-Assembled Monolayers as Substrates for Planar Model Membranes," Biophysical Society, Washington, DC, February 17, 1993.
- Plant, A.L., "Phospholipid-containing Bilayers From Alkanethiol Self-Assembled Monolayers," National Meeting of the American Chemical Society, Denver, CO, March 28, 1993. Invited
- Plant, A.L., "Planar Phospholipid Membrane Electrodes from Self-Assembled Monolayers," (Poster), Society for Biomaterials Annual Meeting: Biotechnology Applications in Biomaterials Workshop, Birmingham, AL, April 28, 1993.
- Plant, A.L., "Model Systems for Cell Surface Interactions," Department of Protein Biochemistry", SmithKline Beecham Pharmaceuticals, King of Prussia, PA, September 30, 1993. Invited
- Poszgay, V., Coxon, B., Glaudemans, C.P.J., Robbins, J.B., and Schneerson, R., "Synthesis and NMR Spectroscopy of Oligosaccharide Fragments of the O-Polysaccharide of Shigella Dysenteriae Type 1," Glycobiology Interest Group Meeting, National Institutes of Health, Bethesda, MD, January 4, 1993.
- Powell, L.J., "Career Skills For a Successful Career In Biotechnology," State of Maryland Tech Prep Meeting, Baltimore, MD, April 19, 1993.
- Powell, L.J., "NIST Role in Providing Standards for Biotechnology," NIST/ASTM Workshop on Standardization Needs in Biotechnology, Gaithersburg, MD, April 26, 1993.
- Powell, L.J., "Overview of NIST Capabilities in Biomaterials and the NIST Advanced Technology Program," Workshop on Biotechnology Application of Biomaterials, Birmingham, AL, April 28, 1993.

- Powell, L.J., "Effective Ways for Collaborating with the Federal Government and Overview of the NIST Advanced Technology Program," Biotechnology Professional Forum, Baltimore, MD, May 6, 1993.
- Powell, L.J., "The NIST Consortium on Advanced Biosensors," Chemical and Biological Sensor Workshop, Pittsburgh, PA, June 11, 1993.
- Reddy, P., "Analysis of the Catalytic and Regulatory Domains of *E. coli* Adenylate Cyclase," Center for Advanced Research in Biotechnology, Rockville, MD, February 11, 1993.
- Reddy, P., "Modification of the pRE Expression Vector to Express Inclusion Bodies as Soluble Proteins: Expression of *E. coli* Adenylate Cyclase," American Society for Biochemistry and Molecular Biology, San Diego, CA, June 1, 1993.
- Reddy, P., "Expression and Regulation of *E. coli* Adenylate Cyclase," Life Technologies, Inc., Gaithersburg, MD, July 14, 1993.
- Reeder, D.J., "Multiple DNA Profiling Techniques Provide Approaches to Human Identification," Mitre Corp., Falls Church, VA, September 15, 1993.
- Reeder, D.J., "Multiple Electrophoretic Approaches to Identify PCR-amplified Genetic Alleles," International Council of Electrophoresis Societies Biennial Conference on Electrophoresis, Oslo, Norway, June 2, 1993.
- Reeder, D.J., "Quality Assurance Testing of Bloodstain Collection Paper," DNA Databanks and Repositories Meeting sponsored by Armed Forces Institute of Pathology, Rockville, MD, May 14, 1993.
- Reeder, D.J., "DNA Profiling and DNA Reference Materials," CSTL Colloquium, NIST, Gaithersburg, MD, April 19, 1993.
- Reeder, D.J., "Reference Material for RFLP Standardization," Second International Symposium on Forensic Aspects of DNA Analysis, Quantico, VA, April 2, 1993.
- Reeder, D.J., "DNA Profiling," Quince Orchard High School, Gaithersburg, MD, March 24, 1993.
- Reeder, D.J., "Panel Discussion on Controversies in DNA Typing," American Academy of Forensic Sciences, Boston, MA, February 19, 1993. Invited
- Reeder, D.J., "NIST To Detect MAGE-1 and Melanin Transform Gene Capabilities," John Wayne Cancer Institute, Los Angeles, CA, February 10, 1993.

- Reeder, D.J., "NIST Development of Separation Methods and Material Standards for PCR-Based DNA Typing," FBI Academy, Quantico, VA, February 8, 1993.
- Reeder, D.J., "Update on NIST's Activities in DNA Profiling Standardization," FBI Academy, Quantico, VA, November 2, 1992.
- Reipa, V., "Application of Dynamic Light Scattering to the Study of Particle Generation at Electrode Surfaces," American Institute of Chemical Engineers 1992 Annual Meeting, Miami, FL, November 5, 1992.
- Reipa, V., "Dynamic Light Scattering in Evanescent Waves," American Physical Society Meeting, Seattle, WA, March 25, 1993.
- Reipa, V., "Raman Spectroelectrochemistry in the Studies of the Biologically Important Molecules," The 14th ITAYA Electrochemiscopy Seminar, Sendai, Japan, August 2, 1993. Invited
- Richie, K.L., "Comparison of Isotopic Detection and Chemiluminescence Results for Standard Reference Material 2390, DNA Profiling Standard," Fourth International Symposium on Human Identification, Scottsdale, AZ, September 27, 1993.
- Schwarz, F.P., "Thermodynamics of Protein-Ligand Interactions," The International Conference on Thermodynamics of Solutions and Biological Systems, New Delhi, India, January 4, 1993.
- Schwarz, F.P., "Thermodynamics of Lectin-Ligand Interactions," The Second Meeting of the Third International Symposium on Biochemical Roles of Eukaryotic Cell Surface Macromolecules, New Delhi, India, January 6, 1993.
- Schwarz, F.P., "Thermodynamics: What Does it Tell us About CRP-cyclic Mononucleotide and Monoclonal Antibody-lysozyme Antigen Interactions?" CARB Seminar, April 1, 1993.
- Schwarz, F.P., Moore, J.L., and McKenney, K.H., "Thermodynamics of Cyclic Mononucleotide Binding to Catabolite Activator Protein and Its Thr-127 -> Leu and Ser-128 -> Ala Mutants," 48th Annual Calorimetry Conference, Duke University, Durham, NC, July 19, 1993.
- Schwarz, F.P., "Applications of Titration Calorimetry to the Study of Biological Systems," Pasteur Institute, CNRS, Paris, France, September 2, 1993.
- Schwarz, F.P. and Poljak, R.J., "Thermodynamics of Lysozyme Antigen-Antibody Interactions," Czechoslovak-French-Polish Conference on Calorimetry and Experimental

- Thermodynamics, Applications to Contemporary Problems, Prague, Czech Republic, September 6, 1993.
- Srinivasan, K., "Capillary Electrophoretic Separations of Polymerase Chain Reaction Amplified DNA Fragments in DNA Typing," 5th International Symposium on High Performance Capillary Electrophoresis, Kissimmee, FL, January 25, 1993.
- Tarlov, M.J. and Plant, A.L., "Ultrathin Amperometric Enzyme Electrodes Based on Biotin-Avidin Coupling at Self-Assembled Alkanethiol Monolayers on Gold," American Institute of Chemical Engineers, Miami, FL, November 6, 1992.
- Tewari, Y.B., "Practical Uses of Biotechnology," Washington Capital Institute of Chemists Meeting, Bethesda, MD, March 18, 1993. Invited
- Tewari, Y.B., "Thermodynamics of the Hydrolysis of L-Tryptophan," 76th Canadian Society for Chemistry, Quebec, Canada, June 2, 1993. Invited
- Tewari, Y.B., "Thermodynamics of the Hydrolysis of Penicillin G and Ampicillin," 48th Annual Calorimetry Conference, Durham, NC, July 22, 1993.
- Weetall, H.H., "Immobilization and Characterization of the Light Sensitive Protein Bacteriorhodopsin," National Research Council of Canada, Montreal, Canada, October 15, 1993. Invited
- Weetall, H.H., "Immobilized Inorganic Biocatalysts, Preparation and Characterization, Mosbach Symposium on Biochemical Technology," Lund, Sweden, December 1, 1992. Invited
- Weetall, H.H., "An Overview of the Consortium on Advanced Biosensors and the National Institute of Standards and Technology," 1993 Biomedical Sensors for Cardiovascular Application Workshop, Durham, NC, February 1, 1993. Invited
- Weetall, H.H., "Immobilized Bacteriorhodopsin as a Possible Adduct for Information Storage and Retrieval," (Poster), 1993 Gordon Research Conference on Analytical Biosensors, Ventura, CA, March 24, 1993. Invited
- Weetall, H.H., "Advanced Biosensor Program at the National Institute of Standards and Technology," 2nd Advanced Research Workshop on Uses of Immobilized Biological Compounds for Detection, Medical, Food, and Environmental Analysis, Brixen, Italy, May 12, 1993. Invited
- Weetall, H.H., "Bacteriorhodopsin Immobilized in Sol-Gel Glass," Biocatalysis: Fundamentals and Applications International Conference, Moscow, Russia, June 7, 1993. Invited



Weetall, H.H., "Biosensor Technology at NIST," Russian Academy of Sciences, Moscow, Russia, July 15, 1993. Invited

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

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

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

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

NMR Spectroscopy of Oligosaccharides Related to Shigella Dysenteriae Type 1, Bruce Coxon  
Univax Biologics, Rockville, MD (CRADA)

The Integration of Crystallization Robotics and the NIST/CARB Biological Macromolecule Database, Gary L. Gilliland  
ICN Biomedicals, Inc. (CRADA)

The Integration of Software and Graphics for Structural Biology on the IBM RISC System/6000 Series Workstations, Gary L. Gilliland  
IBM Corporation (CRADA)

### 4. Patent Awards and Applications

Dukova, T. and Vsevolodov, N., "Photochromic Material" (Submitted March 1993)

Pandey, P.C., "FIA Biosensor for the Analysis of Glucose in Human Serum" (Filed with Patent Office April 1993)

Pandey, P.C. and Weetall, H.H., "Photoelectrochemical Detection of DNA Intercalation" (Submitted August 1993)

Rekharsky, M., "Design and Applications of Fast No-Contact Multichannel Calorimeter with Infrared Thermometer Suitable for Industrial Analytical Determinations in Solutions at Room Temperature" (Submitted May 1993)

5. SRM Activities

None

6. SRD Activities

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

7. Calibrations

None

8. Committee Assignments

**B. Coxon**

ASTM E-13.07 Subcommittee on NMR Spectroscopy (Secretary/Member)  
Washington Area NMR Group (Member)

**J.J. Edwards**

ASTM Committee E-48 on Biotechnology  
Subcommittee on Terminology, ASTM E-48.91 (Chairman)  
Subcommittee on Characterization and Identification of Biological Systems,  
ASTM E-48.02 (Task Group Leader)

**G.L. Gilliland**

Reviewer of SBIR's on Special Study Section 6C of the National Institutes of Health  
Chairman of the NASA Biotechnology Working Group and as such, sit on the  
Microgravity Science and Applications Subcommittee of the Space  
Science and Applications Advisory Committee  
Ad hoc reviewer of DoE and NSF support of the Brookhaven Protein Data Bank,  
December 1992  
Member of the NSF Committee of Visitors reviewing the Biochemistry and Molecular  
Structure and Function Division of Molecular and Cellular Biosciences grant  
review process

Member of the Structural Biology Working Group of the Biotechnology Research Subcommittee (BRS) of the Federal Coordinating Council on Science, Engineering and Technology (FCCSET)

**R.N. Goldberg**

Board of Directors of the Calorimetry Conference (Member)  
IUPAC Commission on Thermodynamics (Titular Member)  
ASTM E-48 Committee on Biotechnology (Member)  
IUPAC Steering Committee on Biophysical Chemistry (Member)  
Evaluation Panel for the Geochemistry Program of the Office of Basic Energy Sciences of the U.S. Department of Energy (Member)  
IUBMB-IUPAC Panel on Biochemical Thermodynamics (Member)

**D.K. Hancock**

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

**J.J. Horvath**

NSF Small Business Innovative Research (SBIR) Review Panel (Member)

**M. Krauss**

DoE Basic Energy Sciences Combustion Research Review, October 13-15, 1992  
Planning for Workshop on Computational Chemistry of Large Molecules to be held in Wroclaw, Poland, June 23-26, 1994

**M.F. McCurley**

Society of the NIST Chapter of Sigma XI Education Committee (Member)  
Biotechnology Research Subcommittee (BRS) of the Committee on Life Science and Health (CLSH) of the Federal Coordinating Council on Science, Engineering and Technology (FCCSET) under the Office of Science and Technology Policy (OSTP) (Executive Secretary/Member)

**K.H. McKenney**

Faculty Search Committee Member, Center for Advanced Research in Biotechnology  
PhD Examining Committee, Department of Genetics, The George Washington University, Washington, DC

**A.L. Plant**

NIST Research Advisory Committee (Member)

**L.J. Powell**

FCCSET Biotechnology Research Subcommittee (Chair)  
Technology Transfer Working Group (Chair)  
Advisory Committee, NIH Women's Health Initiative (ex officio member)  
ASTM E-48 (1st Vice Chair)  
CARB Board of Overseers  
ACS Committee on Chemical Abstracts Service (Chair)  
ACS Biochemical Technology Division (Councilor)  
ACS Committee on Budget and Finance  
Women Chemists Committee  
NIST Liaison to ACS  
Board of Managers, Chemical Society of Washington

**P. Reddy**

PhD Examining Committee, Department of Genetics, The George Washington University, Washington, DC  
Served on the Committee for ATCC to Evaluate Several Expression Vectors in the ATCC Catalogue

**D.J. Reeder**

ASTM E-48 on Biotechnology  
Advisory Committee for the Institute of Forensic Anthropology and Human Identification  
CAP Forensic Identity/Parentage DNA Proficiency Testing Task Force  
Electrophoresis Society (President)  
NIST Animal Care and Use Committee  
NCCLS Area Committee on Molecular Methods  
Technical Working Group on DNA Analysis Methods (TWGDAM) Quality Assurance Subcommittee

**F.P. Schwarz**

NSF Review Committee for Proposals submitted to the Division of Molecular and Cellular Biosciences  
NIH/ADAMHA Scientific Review Committee  
Session Organization Committee for 50th US Calorimetry Conference to be held at NIST in 1995  
Review Committee for Proposals submitted to the NIST Cold Neutron Research Facility  
IUPAC exploratory sub-committee on Data Base of the Thermodynamic Stabilities of Natural and Mutant Proteins  
Promotion and Tenure Review Committee of the Center for Advanced Research in Biotechnology  
Center for Advanced Research in Biotechnology Ib Space Committee Washington  
Editorial Review Board

## 9. Editorships

**M.M. Dizdaroglu**

Free Radical Research Communications

**D.J. Reeder**

Applied and Theoretical Electrophoresis

**H.H. Weetall**

Applied Biochemistry and Biotechnology (Executive Editor)

## 10. Seminars

**October 5, 1992**

Dr. Dennis Torchia, Bone Research Branch, NIDR/NIH, Bethesda, MD, "NMR Structural Studies of TGF $\beta$ 1 and 3-Glucose." (Division Sponsor: G.L. Gilliland)

**October 9, 1992**

Dr. Michael James, Department of Biochemistry, University of Alberta, Alberta, Canada, "The Convergence of Active Site Geometries Among the Four Classes of Proteolytic Enzymes." (Division Sponsor: G.L. Gilliland)

**October 26, 1992**

Dr. Ken Johnson, Department of Molecular and Cell Biology, Pennsylvania State University, State College, PA, "Mechanism of HIV Reverse-Transcriptase." (Division Sponsor: G.L. Gilliland)

**October 29, 1992**

Dr. Steffen Loft, Department of Pharmacology, University of Copenhagen, Copenhagen, Denmark, "8-Hydroxydeoxyguanosine as a Biomarker of Oxidative DNA Damage." (Division Sponsor: M.M. Dizdaroglu)

**November 2, 1992**

Dr. Donald Creighton, Department of Chemistry, University of Maryland, Baltimore, MD, "Inhibition of Glyoxalase I by Ene Diol Analogues: The Mechanistic Basis of a Tumor-Selective Anti-Cancer Strategy." (Division Sponsor: G.L. Gilliland)

**November 9, 1992**

Dr. Susan Keating, Syva Company, San Jose, CA, "Nanosecond Fluorescence Microscopy." (Division Sponsor: H.H. Weetall)

**November 16, 1992**

Dr. Earle Stellwagen, Department of Biochemistry, University of Iowa, Iowa City, IA, "C-13 NMR Measurements of Residue-Helical Content in Model Peptides." (Division Sponsor: G.L. Gilliland)

**November 20, 1992**

Dr. Aridzei Rubin, Moscow State University, Moscow, Russia, "Conformational Changes in Primary Photosynthesis and the Bacteriorhodopsin Photocycle." (Division Sponsor: H.H. Weetall)

**November 23, 1992**

Dr. Philip Ross, Laboratory of Molecular Biology, NIADDK/NIH, Bethesda, MD, "Interactions in the Major Groove of DNA: Thermodynamics of Protein-Nucleic Acid and Polynucleotide Triple-Helix Formation." (Division Sponsor: F.P. Schwarz)

**November 30, 1992**

Dr. Shosuke Kawanishi, Faculty of Medicine, Kyoto University, Kyoto, Japan, "Active Oxygen Formation and DNA Damage by Interaction of Metals and Carcinogens." (Division Sponsor: M.M. Dizdaroglu)

**November 30, 1992**

Dr. Ed Lattman, Department of Biophysics, Johns Hopkins University, Baltimore, MD "What is the Dielectric Constant Inside a Protein?: An Experimental Approach." (Division Sponsor: G.L. Gilliland)

**December 7, 1992**

Dr. Peter Coleman, Division of Biomolecular Engineering, CSIRO, Australia, "Influenza Virus Neuraminidase: Enzyme, Antigen and Therapeutic Target." (Division Sponsor: G.L. Gilliland)

**December 11, 1992**

Dr. Haygen Bayley, Worcester Foundation for Experimental Biology, Shrewsbury, MA, "Assembly of Membrane-Bound Proteins." (Division Sponsor: J.J. Kasianowicz)

**December 14, 1992**

Dr. Catherine Fenselau, Department of Chemistry, University of Maryland, Baltimore, MD, "Primary Structures and Other Physical Chemical Properties of Proteins Studied by Mass Spectrometry." (Division Sponsor: G.L. Gilliland)

**January 21, 1993**

Dr. William Line, Miller Brewing Company, Milwaukee, WI, "Use of Rice Pullulanase in Syrup Manufacture." (Division Sponsor: H.H. Weetall)

**January 25, 1993**

Dr. Carl Wu, NIH, Bethesda, MD, "Induction of the Heat Shock Response." (Division Sponsor: G.L. Gilliland)

**February 22, 1993**

Dr. A.J. Carpousis, Department of Molecular Biology, University of Geneva, Geneva, Switzerland, "RNase E Mediated mRNA Processing and Degradation in *E. coli*: Specificity of the Nuclease and Purification of a Protein Complex Containing RNase E and Polynucleotide Phosphorylase." (Division Sponsor: G.L. Gilliland)

**March 11, 1993**

Dr. Michael Rossmann, Department of Biological Sciences, Purdue University, West Lafayette, IN, "Aspects of Virus Structure." (Division Sponsor: G.L. Gilliland)

**March 15, 1993**

Dr. Robert Ashton, Cornell University, Cornell, NY, "Binding Interactions in the Thrombin-Fibrinogen & Thrombin-Factor VIII Systems as Studied with BIAcore Technology." (Division Sponsor: H.H. Weetall)

**March 18, 1993**

Dr. Steen Steenzen, Max-Planck Institute, Mulheim, Germany, "Electron-Transfer Reaction with and between Nucleic Acid Bases." (Division Sponsor: M.M. Dizdaroglu)

**March 22, 1993**

Dr. Arthur Landy, Division of Biological Medicine, Brown University, Providence, RI, "Higher Order Structures in Lambda Site Specific Recombination." (Division Sponsor: K. McKenney)

**March 29, 1993**

Dr. Randy Read, Department of Medical Microbiology and Infectious Diseases, University of Alberta, Alberta, Canada, "Crystal Structure Studies of Bacterial Toxins." (Division Sponsor: G.L. Gilliland)

**April 5, 1993**

Dr. Alexander McPherson, Department of Biochemistry, University of California/Riverside, Riverside, CA, "The Structure of Satellite Tobacco Mosaic Virus." (Division Sponsor: G.L. Gilliland)

**April 12, 1993**

Dr. Brian Reid, Department of Chemistry, University of Washington, Seattle, WA, "Structures of Some Interesting Nucleic Acid Duplexes in *Solution*." (Division Sponsor: G.L. Gilliland)

**April 26, 1993**

Dr. Peter Privalov, Department of Biology, Johns Hopkins University, Baltimore, MD, "New Developments in Microcalorimetry." (Division Sponsor: F.P. Schwarz)

**May 3, 1993**

Dr. Martin Rosenberg, Vice President, Director, Biopharmaceutical Research and Development, SmithKline Beecham Pharmaceuticals, King of Prussia, PA, "Antiviral Strategies Using HIV Molecular Targets." (Division Sponsor: K. McKenney)

**May 4, 1993**

Dr. David Vanderah, Naval Air Warfare Center Weapons Division, China Lake, CA, "Approaches to New Non-polluting Anti-fouling Technology and Minor Component Analysis of a New Energetic Material." (Division Sponsor: H.H. Weetall)

**May 7, 1993**

Dr. Michael Thompson, University of Toronto, Toronto, Canada, "Biological Species at Liquid-Solid Interfaces." (Division Sponsor: A.L. Plant)

**June 22, 1993**

Dr. Jerry W. King, U.S. Department of Agriculture, Washington, DC, "Solubility of Lipids in Super Critical Fluids - Process and Analytical Applications." (Division Sponsor: L.J. Powell)

**June 29, 1993**

Dr. Jonathan Dordick, University of Iowa, Iowa City, IA, "Biocatalysis in Organic Media." (Division Sponsor: H.H. Weetall)

**July 7, 1993**

Dr. Michael M. Domach, Carnegie Mellon University, Pittsburg, PA, "Extracting Information Without Extracts and Validating Protein Isolates." (Division Sponsor: L.J. Powell)

**July 14, 1993**

Dr. Vincent L. Vilker, University of California, Los Angeles, CA, "Biocatalysts by P-450 Redox Enzymes." (Division Sponsor: L.J. Powell)

**July 15, 1993**

Dr. Horst H. Klump, Department of Biochemistry, University of Cape Town, Republic of South Africa, "Folding of DNA into Tertiary Structures." (Division Sponsor: F.P. Schwarz)



**July 19, 1993**

Dr. Moses Schanfield, Analytical Genetic Testing Center, Denver, CO, "Development and Implementation of PCR based Amplified Fragment Length Polymorphisms (AFLPs) for Forensic Applications." (Division Sponsor: D.J. Reeder)

**July 21, 1993**

Dr. Ali Cinar, Illinois Institute of Technology, Chicago, IL, "Process Models for Monitoring, Diagnosis and Control of Bioprocesses." (Division Sponsor: A.K. Gaigalas)

**July 28, 1993**

Dr. Vitali Silin, Institute of Biochemistry, Vilnius, Lithuania (NIST Guest Researcher), "Application of Surface Plasmons in Biomolecular and Humidity Sensors." (Division Sponsor: A.K. Gaigalas)

**August 4, 1993**

Dr. Howard Brenner, Massachusetts Institute of Technology, Cambridge, MA, "Macrotransport: Applications to Chromatographic, Electrophoretic and Polymetric Transport." (Division Sponsor: J.B. Hubbard)

**August 13, 1993**

Dr. John Luong, National Research Council, Quebec, Canada, "Some Contributions of Cyclodextrins in Mediated Biosensors and Enzyme Assays." (Division Sponsor: H.H. Weetall)

**August 18, 1993**

Dr. David Stenger, Naval Research Laboratory, Washington, DC, "Lithographic Definition of Neuronal Microcircuits." (Division Sponsor: A.L. Plant)

**September 2, 1993**

Gaoyi Xiao, Department of Chemistry, University of Oklahoma, Norman, OK, "Conformational Studies and Free Energy Calculation of a Ferric Complex of Hexadentate 3-hydroxy-2-pyridinone (FeCP130) and Its Two Analogs by MM and MD/FEP Simulations." (Division Sponsor: G.L. Gilliland)

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

**October 9-22, 1992**

Co-organizer and instructor of Macromolecular Crystallography, a Cold Spring Harbor Laboratory Workshop, Cold Spring Harbor, NY (G.L. Gilliland)

**April 26-27, 1993**

Chaired NIST/ASTM Workshop on Standardization Needs in Biotechnology, NIST, Gaithersburg, MD (L.J.Powell)

**April 28, 1993**

Co-sponsored Workshop on Biotechnology Applications in Biomaterials, Birmingham, AL (L.J.Powell)

**April 30, 1993**

Co-sponsored the Washington Area NMR Group Minisymposium, National Institutes of Health, Bethesda, MD (B. Coxon)

**June 8-10, 1993**

Co-chairman of the Mid-Atlantic Protein Crystallography Workshop, Johns Hopkins University, Baltimore, MD (G.L. Gilliland)

**July 7-9, 1993**

Organized Workshop, "Small Genomes: New Initiatives in Mapping and Sequencing" at the Center for Advanced Research in Biotechnology, National Institute of Standards and Technology, Rockville, MD, supported by the Office of Health and Environmental Research, Department of Energy (K. McKenney)

**July 12, 1993**

Chaired a session at the 4th European Symposium on Organic Reactivity: Physical and Biological Aspects, Newcastle-Upon-Type, England (B. Coxon)

**September 19-22, 1993**

Co-sponsored Frontiers in Bioprocessing III, Boulder, CO (L.J. Powell, K.D. Cole)

**September 20-23, 1993**

Co-sponsored International Conference on Molecular Electronics and Biocomputing, NIST, Gaithersburg, MD (L.J. Powell)

## II. Chemical Kinetics and Thermodynamics Division (833)

Sharon G. Lias, Chief

### A. Division Overview

Processes involving chemical change can only be predicted and controlled if the kinetics and thermodynamics of the reactions are known and understood. Thermodynamics has the goal of predicting the feasibility or spontaneity, and the equilibrium yields, of any chemical process from a knowledge of the energetics of the chemical transformations. Chemical kinetics is the study of the rates of chemical reactions, the factors which influence those rates, and the detailed mechanisms of the reactions. A detailed understanding of the energetics and mechanisms of chemical change is at the very heart of chemistry and an important goal of science. Societal applications of -and needs for - data on the chemical thermodynamics and kinetics of compounds and processes are numerous and diverse. These include understanding and modeling any system where chemical change is important, such as combustion processes, effects of pollutants on the earth's atmosphere, industrial chemical processing, biological and medical processes, and synthesis of materials.

The programs of the NIST Chemical Kinetics and Thermodynamics Division include experimental measurements of kinetic and thermodynamic quantities, the development of measurement techniques and methodologies, and the development and certification of Standard Reference Materials (SRMs). However, 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, that is, Standard Reference Data. There are four specialized Data Centers within the Division (Chemical Thermodynamics, Chemical Kinetics, Ion Kinetics and Energetics, and Mass Spectrometry), as well as several database-development projects, all sponsored by the Standard Reference Data Program. The Division also has a strong expertise in the generation of expert software for use with chemical databases. It is a part of the National Institute of Standards and Technology (NIST) mission to collect, compile, critically evaluate, and disseminate evaluated technical data.

The tie between the experimental programs and the work of the Data Centers is very strong, with many Division scientists actively engaged in both experimental and data evaluation projects. Because, the expertise and insight needed for reliable data evaluation are best obtained from scientists who are experienced in experimental work, 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.

Users of Division databases originate primarily from industry (65%), with other users coming from academic (14%), federal, state, and local government (13%), and other (7%) laboratories.

Industrial database customers include companies from the chemical, pharmaceutical, food and beverage, rubber, petroleum, communications, aerospace, and computer industries, as well as hospitals, environmental laboratories, and other businesses. Government users include state and local law enforcement agencies, drug testing laboratories, and all the federal government agencies which have laboratory facilities (Agriculture, Food and Drug, Fish and Wildlife, Federal Bureau of Investigation, National Institutes of Health, the Environmental Protection Agency, the Department of Energy, etc.)

The Division is administratively divided into three groups, the Experimental Chemical Kinetics Group, the Kinetics Data Centers Group, and the Chemical Thermodynamics Group. The work of the latter Group includes both experimental and data evaluation activities in the area of thermodynamics. There is a significant degree of overlap between the technical activities of the three Groups, with individual scientists often carrying out collaborative assignments which cross Group lines. During 1993, two highly respected Division senior scientists who were serving as Group Leaders retired. Dr. Pierre Ausloos, a NIST Fellow and formerly the Director of the Center for Chemical Physics, was acting as the Group Leader for Experimental Chemical Kinetics, and Dr. John Herron, who at one time served as Chief of the Chemical Kinetics Division, headed the Kinetics Data Centers Group. Dr. Ausloos has been replaced as Group Leader by Dr. Pedatur Neta, and Dr. W. Gary Mallard now heads the Kinetics Data Centers Group. Dr. Neta is a well-known radiation chemist and liquid phase kineticist, and Dr. Mallard is a leader in the development of specialized chemical databases.

The focus of both experimental and Data Center programs in the Division is largely determined by national needs in areas where chemical kinetics and thermodynamics data are important, that is, by the needs of the various communities which are served by Division programs. The Chemical Kinetics and Thermodynamics Division serves as a technical resource for a wide range of external activities and programs. These activities in support of other programs are an integral part of our mission, and a key means of applying our scientific expertise to the solution of industrial, environmental, defense, and energy-related problems. In 1993, 32% of Division research was supported by other agencies, notably including the Department of Energy (DoE), the National Aeronautics and Space Administration (NASA), the Environmental Protection Agency (EPA), and the Department of Defense (DoD). Another 26% of Division work was supported by the Standard Reference Data Program (SRDP). At the present time, most of the on-going work, including both experimental and data evaluation activities, is relevant to **environmental concerns, energy, industrial processes, and/or analytical chemistry.**

The Division has a long history of participation in activities associated with **atmospheric chemistry**. Work on 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 the panel which provides the definitive recommendations of data for modeling stratospheric chemistry, NASA's Upper Atmosphere Research Program, and the Scientific Steering Committee of the International Network for the Detection of Stratospheric Change.

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. 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. This work is supported by NASA and the EPA.

Important long-term projects dealing with **energy-related** issues include the DoE-sponsored experimental work aimed at understanding solar energy storage mechanisms, and a data evaluation project concerned with the kinetics of combustion processes, also sponsored by DoE. The goal of this project is the production of a complete, self consistent evaluated data base of kinetic data for use in the modeling of hydrocarbon combustion. Also during 1993, the Division's oxygen-bomb calorimetry laboratory certified four energy-related SRMs for use by the coal-fired power utility companies.

Other Division research is oriented towards problems related to **industrial processes**. Current work in the Division includes the development of detection techniques for use in chemical processing in the Division's state-of-the-art resonance-enhanced multiphoton ionization (REMPI) laboratory, the development of a database for dry etching and semiconductor manufacture, and unique calorimetric measurements relevant to advanced manufacturing. During 1993 work was initiated to set up a new facility to exploit degenerate four wave mixing spectroscopy as a means of measuring 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. Experimental work using the facility will be initiated in 1994, in collaboration with scientists from Stanford University.

Division involvement with **analytical chemistry**-related projects goes back many years. Research carried out in these laboratories in the 1960's laid the basis for the development of an analytical technique now called Chemical Ionization Mass Spectrometry; the early research program has evolved into a project now fully funded by DoE on mass spectrometric studies of the mechanisms and thermochemistry of chemical ionization processes.

The project in the Division which probably has the widest visibility outside of NIST is the maintenance and improvement of the NIST/EPA/NIH Mass Spectral Database, a large database of electron mass spectra which is in use in thousands of analytical chemistry laboratories throughout the world. The collection of spectra is distributed to the instrument manufacturers who distribute the database in the data systems of commercial analytical mass spectrometers. The Data Center also produces a personal computer version with search software which is

marketed by the Standard Reference Data Program. 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. For example, Dr. Stephen E. Stein maintains active collaborations with programmers from most major instrument companies (such as Hewlett-Packard and Perkin Elmer) to aid in implementing software developed at NIST for the improvement of the reliability of library searching in commercial mass spectrometers.

Except for the mass spectral database, perhaps the best known computer-based database product generated in the Division is the Chemical Kinetics Database, which provides an output mechanism for the combustion and upper-atmosphere data evaluation projects; this database has sold more copies - nearly 1200 - than any other single personal computer database distributed by the SRDP. This year, Version 5.0 of the product was released.

Division scientists are in the forefront of work on the **development of software for use with personal computer-based chemical databases**. The professional quality of this software is such that Division scientists are in demand for collaboration on database-development projects originating outside the Division. For example, this year a new database, the Liquid Phase Kinetics Database, was produced by Dr. W. Gary Mallard in collaboration with the Notre Dame Radiation Laboratory. Bio-Rad's Sadtler Division, a leading commercial supplier of databases of infrared and nuclear magnetic resonance (NMR) spectra, concluded a new Cooperative Research and Development Agreement (CRADA) with us for the development of expert software for use with chemical databases. In recognition of our leadership in this area, Drs. Stephen E. Stein and W. Gary Mallard were given NIST Measurement Services Awards for their contributions to the Standard Reference Data Program, Dr. Sharon Lias was invited to organize a symposium entitled "Spectroscopic Databases: Computer Innovations for Search and Interpretation" at the American Chemical Society National Meeting. The symposium took place in August, with Dr. Stephen E. Stein as one of the plenary speakers.

The Third International Conference on Chemical Kinetics was held at NIST on July 12-17, 1993, under the sponsorship of the Division. The conference, subtitled "Reactions in Gas and Condensed Media" was attended by 224 scientists from over 20 countries. The first two conferences in this series were also organized by Division members and held at NIST in 1985 and 1989. Dr. Robert E. Huie was the principal organizer of the 1993 meeting. The focus of the meeting was the generation and use of chemical kinetic data in both gas and condensed phase systems. Subjects discussed included theory and dynamics, and the applications of chemical kinetics such as atmospheric chemistry and chemical vapor deposition.

A workshop entitled "Industrial Applications of Computational Chemistry", organized by Drs. Wing Tsang and Michael Zachariah (Div. 836) was held at NIST on May 19-20, 1993. Representatives from Air Products, Shell Development, Dow, DuPont, Exxon, Sandia, and the Army Research Laboratory met with Chemical Science and Technology Laboratory staff

members to discuss the impact of recent advances in computational chemistry on the process industries. Industry representatives emphasized that the increased computational capabilities now available permit more fundamental approaches to process design, and that widespread industrial use of computational tools would increase American competitiveness. Attendees from industry stated that they look to NIST to provide much of the fundamental data which would underlie the successful implementation of such an approach on a wide scale.

Division scientists continue to hold major leadership positions in the fields of chemical kinetics and thermodynamics. Drs. P.A.G. O'Hare and John Herron serve as chairmen of the International Union of Pure and Applied Chemistry (IUPAC) Commissions on Thermodynamics and on Kinetics, respectively, while other Division members are secretaries of committees of those Commissions. Dr. O'Hare is the Editor-in-Chief of the Journal of Chemical Thermodynamics. Drs. Robert F. Hampson and Michael J. Kurylo are members of the NASA Panel for Data Evaluation which recommends definitive values of numeric data for modeling stratospheric chemistry. Dr. Kurylo is Acting Manager of NASA's Upper Atmosphere Research Program and Chairman of the Scientific Steering Committee of the International Network for the Detection of Stratospheric Change, with a wide range of scientific management and international scientific assessment responsibilities. 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).

The vitality of Division programs is also evidenced by the large numbers of national and international collaborations. For example, Dr. Jeffrey Hudgens collaborated this year with Prof. M.N.R. Ashfold of the University of Bristol, U.K., to discover and analyze resonant enhanced multiphoton ionization spectra of radicals. Dr. P.A.G. O'Hare maintains active collaborations on the determinations of the thermodynamic properties of materials with scientists from Argonne National Laboratory, Colorado State University, Griffith University in Australia, the Max-Planck Institute in Stuttgart, Germany, the University of New Brunswick, and the Royal Military College in Kingston, Canada. Dr. Wing Tsang collaborates actively with kineticists at the Catholic University of America, and Dr. Pedatsur Neta continues his long-term collaborations with scientists from Howard University, the Fast Kinetics Center in Austin, Texas, and Ben Gurion University in Israel. Twenty senior scientists from 13 countries spent some time in Division laboratories as Guest Researchers, and two academic scientists chose to spend sabbatical years here.

Next year will see significant new efforts in the development of **estimation methods** to allow the prediction of data for species for which no experimental measurements have been made. These new activities encompass a wide variety of approaches to the universal problem of predicting chemical properties and processes - high level *ab initio* calculations, the development and evaluation of algorithms for computational chemistry, and the further development of simple schemes for the prediction of chemical and physical properties from molecular structure. Algorithm development for the analytical chemistry databases maintained in the Division will

similarly focus on the prediction of spectra which have never been experimentally determined. New experimental programs now being initiated, such as the degenerate four-wave mixing project and a new facility for determining the properties of aqueous electrolyte solutions at low temperatures, will develop with a sharp focus on the needs of U.S. industry.



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

**1. Stability of Halocarbons in the Atmosphere**

**M.J. Kurylo, R.E. Huie, T.J. Buckley, A. Fahr, B. Laszlo (Hungarian Academy of Science, Hungary), P. Maruthamuthu (Madras University, India), A.K. Nayak (Bhaba Atomic Research Center), R.D. Saini (Bhaba Atomic Research Center, India), and Z. Zhang (Catholic University of Leuven, Belgium)**

This program, supported by NASA and EPA, focusses on the study of the gas phase kinetics and photochemistry of important atmospheric constituents. The research emphasizes those processes relevant to the fate of natural and anthropogenic trace gases in the troposphere and their chemical role in altering stratospheric composition. Major goals of this work include predicting the impact of human activities on stratospheric ozone and on global climate.

Current activities continue to be directed at the measurement of rate constants for the reactions of OH radicals with compounds being considered by industry as replacements for fully halogenated CFCs. The flash photolysis resonance fluorescence apparatus has been modified to accommodate a commercial flash lamp with better flux reproducibility than previously available. This change has permitted improved optical coupling of all components for improved detection sensitivity and signal to noise level. A laser photolysis resonance fluorescence apparatus has been designed and fabricated and is now operational. This facility, together with the flash photolysis apparatus, now offers better photochemical control of radical production.

During the past year, manuscripts have been published on the kinetics of reactions of OH with several partially fluorinated ethers (one of which is under consideration as a replacement for the primary cooling fluid being used in the U.S. gaseous diffusion process for uranium isotope enrichment), selected hydrofluorobutanes, and methyl bromide (which is widely used internationally as a soil and commodity fumigant). These papers also report the development of a coarse reactivity scale that may be useful in estimating the atmospheric lifetimes for some of the molecules for which laboratory kinetic data do not exist. Manuscripts are also being prepared on the atmospheric reactivity of methane, trifluoromethane, and several partially fluorinated propanes.

Measurements of the ultraviolet absorption cross-sections of CFC alternatives are continuing. 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, and 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. At the longer ultraviolet wavelengths (where the light flux is high and absorption can be important), the cross sections are so low that measurements are difficult and unreliable. Work reported last year demonstrated that absorption

coefficients measured in the liquid phase (where the high density permits the achievement of higher optical depths for a given path length than those attainable in the gas phase) can be reliably converted to the corresponding gas phase coefficients. A manuscript detailing a study of absorption cross sections of HCFC-141b ( $\text{CH}_3\text{CFCl}_2$ ) using this approach is in press, and studies of  $\text{CF}_3\text{CCl}_2\text{H}$  (HCFC-123),  $\text{CF}_3\text{CFCIH}$  (HCFC-124), and  $\text{CH}_3\text{CCl}_3$  were also completed. The work quantitatively addresses the role of small levels of scattered light in the measurement of small absorption cross sections and thereby offers an explanation for discrepancies in the literature. A temperature-controlled cell was designed, constructed, and tested, to permit studies of the temperature dependences of the absorption cross sections; the unique design of the cells and the vacuum chamber allows sequential use of the gas or liquid phase cells without modification of the apparatus or disruption of the vacuum.

Dr. M.J. Kurylo was invited by the Scientific Steering Group of the 1994 United Nations Environment Program Assessment of Ozone Depletion to be a contributing author on a chapter on methyl bromide. The purpose of this chapter is to update the information contained in the 1992 interim report, "Methyl Bromide and the Ozone layer: A Summary of Current Understanding," for which Dr. Kurylo was also a contributing author.

Two papers have also been published detailing the results from collaborative studies concerning the OH reactivity with proposed automotive fuel additives, a joint study with researchers at the Ford Motor Company.

Studies of the fate of the CFC-replacement compounds have been expanded to consider the reactions of secondary products. One vexing problem has been the ultimate fate of trifluoroacetic acid. This compound is highly soluble in atmospheric droplets, but its subsequent reactions are not known. To elucidate this chemistry, we have carried out studies of the aqueous-phase reactions of this compound and the other fluoro- and chloroacetates. First, the rate constants for the reactions of a number of free radicals likely to be important in atmospheric droplets were determined for these acetates, then the rate of photodecarboxylation of the acetates, complexed to ferric ions, was measured. In all cases, the trifluoroacetate was very unreactive. For the other acetates, however, these mechanisms might have atmospheric importance.

## 2. Kinetics Data Evaluation and Database Production: The Chemical Kinetics Data Center

**W.G. Mallard, W. Tsang, R.F. Hampson, J.T. Herron, K.K. Irikura, R.D. Levin, D. Frizzell, P. Christian, and J. Reed**

The Chemical Kinetics Data Center is responsible for evaluating data on the chemical kinetics of atmospheric reactions involving halogenated species for the NASA Panel for Data Evaluation. Dr. Robert Hampson of the Data Center and Dr. Michael Kurylo, researcher in the experimental programs of the Division, are members of this panel, which provides the definitive evaluated data

for use in modeling the chemistry of the upper atmosphere. This year, estimated values of the ozone depletion potential for more than 500 hydrochlorofluorocarbons and hydrobromofluorocarbons were provided for the Ozone Secretariat of the United Nations Environment Program. Dr. Hampson is also a member of the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. For this organization, the Chemical Kinetics Data Center has the primary responsibility for evaluation of the chemical kinetic and photochemical data for reactions of halogenated species and selected oxygenated species.

A long-range Data Center program, supported by the Department of Energy, is directed at producing a complete database of self-consistent, evaluated kinetic data for use in the modeling of hydrocarbon combustion. The goal is an evaluated database covering all data pertinent to combustion of the  $C_1$ - $C_4$  alkanes and methanol. A related effort sponsored by the JANNAF Panel for Propellant Combustion involves the evaluation of similar data for propellant combustion processes. The evaluation of thermal rate data important for combustion phenomena is closely tied to Dr. Tsang's program of experimental studies described elsewhere under the heading "Combustion Chemistry". Earlier publications generated under the Combustion Chemistry project dealt with reactions involving methane, methanol, propane, n-propyl and isopropyl radicals, isobutane, t-butyl and isobutyl radicals, propene, allyl radicals, 2-butene and 2-butenyl. Current work involves interpretation of data on reactions involving butadiene and butadienyl.

This year, both experimental and data evaluation programs included work on understanding how fire suppressants work. A project was carried out to develop through simulation, a process for the destruction of  $CF_3Br$  (Halon 1301). There are large stocks of this fire retardant which must be disposed of because of the deleterious effects of such brominated methanes on the earth's ozone layer.

Another calculational project, carried out in collaboration with Dr. M. Zachariah of the Process Measurements Division, involved an examination of the chemistry of conversion of silane to silicon oxides in a flame. Such processes are of importance to materials synthesis. The analysis is based on quantum chemical calculations, the results of which are applied to the derivation of kinetic information.

The single most important dissemination mechanism for Data Center collections 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. The package has sold more than 900 copies since its release, making it the best-selling personal computer database distributed by the Standard Reference Data Program. Version 5.0 of the Chemical Kinetics Database, containing over 20,000 records relating to over 6600 reactant pairs, was released during 1993. The total number of chemical species for which data are included has been increased to 3000. Work on this update included some software improvements, and extensive examinations of the database for errors and inconsistencies.

The new solution kinetics database, developed in collaboration with Notre Dame Radiation Laboratory (NDRL) and Division members R. E. Huie and P. Neta, was released in October 1992. The database contained more than 10,300 rate determinations for over 7800 reactions. The number of chemical species which are either products or reactants was 6400. Citations from over 2200 references were included. The first update, scheduled to be released in October 1993, will include new search modes and many additional reactions.

3. Chemical Thermodynamics Data Evaluation and Database Production - Inorganic Compounds and Aqueous Solutions: The Chemical Thermodynamics Data Center

D.B. Neumann, P.A.G. O'Hare, D.G. Archer, D.V. Tchekhovskoi (Institute for High Temperature, Russia), R.D. Levin, D. Frizzell, P. Christian, and J. Reed

There is a revival of interest in transition-metal disilicides as interconnects and gate materials in very-large-scale integrated circuits; considerable effort has been expended in the preparation and measurement of the electrical properties of thin films of these disilicides, but much less attention has been paid to their thermodynamic properties. Without good thermodynamic information for these materials, any long term compatibility evaluation is of little value. This year, a survey of the thermodynamic properties of the disilicides of tungsten, molybdenum, tantalum, titanium, cobalt, and nickel and platinum monosilicide was carried out and prepared for publication in the Journal of Physical and Chemical Reference Data. Another data evaluation article presented statistical thermodynamic calculations combined with the results of high temperature Knudsen-effusion studies of the vaporization of silicon sesquioxide,  $\text{Si}_2\text{O}_3$ , to calculate thermodynamic properties of  $\text{SiTe}$  from 0 to 2000 K. A critical assessment of the thermodynamic properties of  $\text{PtSi}$  was also completed.

In 1993, the database, "Properties of Aqueous Solutions" (subtitled "Aqueous Solutions of Electrolytes: Binary and Mixed Electrolyte Systems - Activity and Osmotic Coefficients, Excess Gibbs Energy") was submitted to the Standard Reference Data Program for release. This database was prepared under the sponsorship of the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers.

A computer file of the "NBS Tables of Chemical Thermodynamic Properties of Inorganic Substances" was formatted and extensive error checking was carried out preparatory to the production of a distributable personal computer database.

The project, "JANNAF Thermochemical Tables for Species of Importance to Ozone Depletion," being carried out in collaboration with Malcolm 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, experimental spectroscopic and thermodynamic data was gathered for radicals containing

F, Cl, Br, N, O, and/or H which are of interest to stratospheric ozone depletion processes. In order to facilitate the evaluation of these data, existing algorithms for the computation of the thermal functions for gas phase diatomic molecules were revised to increase the accuracy of the computations. Programs for computing the thermal functions of polyatomic molecules were also revised to include more detailed rotational and spin-rotational interactions.

#### 4. Combustion Chemistry

**W. Tsang, J. Manion, and V.I. Babushok (Russian Academy of Sciences, Russia)**

This project is devoted to the development of a fundamental quantitative understanding of high temperature reactions of organic compounds, with the long-range goal of developing 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. Selection of specific systems for study is largely guided by the affiliated data evaluation effort described above (under 2: Chemical Kinetics Data Evaluation and Database Development), with an emphasis on obtaining results which are needed to develop and validate correlation schemes for the prediction of rate expressions.

This year, the focus was expanded to encompass studies aimed at providing a fundamental understanding of how fire suppressants work. A study of the reaction of H-atoms with  $\text{CF}_2\text{ClCF}_2\text{Cl}$  was completed. It was found that hydrogen atoms react with the chlorine atoms 50-100 times faster than with the F-atoms even at high temperatures. Experiments were also carried out to generate the rate expressions for all reaction channels of fluorinated methyl radicals reacting with other methyl radicals; about 100 rate expressions were obtained for stabilization, elimination and H-ejection channels.

The experiments in liquid phase pyrolysis, aimed at developing a more fundamental understanding of the mechanism of dioxin formation during incineration processes, were concluded. A chapter entitled "Dioxins and Furans" was submitted for publication in a book entitled "Handbook of Waste Incineration."

#### 5. Solar Energy Conversion and Storage

**P. Neta, J. Grodkowski (Institute of Nuclear Science, Warsaw, Poland), S. Marguet (Centre National de Recherche Scientifique, France), and E.N. Natarajan (University of Madras, India)**

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, utilizing metalloporphyrins as photosensitizers.

This year redox and alkylation reactions of metalloporphyrins that may be important in their use as catalysts for various processes were elucidated. A study of several metalloporphyrins (Ni, Cr, Fe, Mn) reduced at the metal center and reactions with radicals that may lead to formation of metal-carbon bonds (leading to species that may play an important role in catalysis) has been published. Other studies on porphyrins that were completed and published during the year involve the reduction of copper porphyrins (where, surprisingly, despite the fact that the electron was added to the ligand, the intermediate underwent rapid demetallation) and the steric effects of substituents on the mechanism of reduction of various metalloporphyrins (where bulky substituents at the ortho positions were found to retard protonation of the anion radical and thus lead to formation of chlorins rather than phlorins). Other work explores the possibility of reducing CO<sub>2</sub> by a reduced metalloporphyrin and inserting CO<sub>2</sub> into a metal-carbon bond, which would convert the gas into an organic material.

## 6. Aqueous Free Radical Kinetics: Experimental Studies and Data Compilation

**R.E. Huie, P. Neta, S. Padmaja (Indian Institute of Technology, India), P. Maruthamuthu (Madras University, India), 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. A knowledge of the aqueous chemistry of organic peroxy radicals is needed for understanding the biological activity of these radicals, and for assessing the potential toxicity of industrially important compounds.

The long-term project on the investigation of the kinetics and activation parameters for reactions of inorganic radicals continued. Determinations were made of the rates of reaction of halogen radicals, SO<sub>4</sub><sup>•-</sup> and NO<sub>3</sub><sup>•</sup> in various aqueous/organic mixtures, and temperature and solvent effects on the kinetics were observed. Reactions studied include electron transfer reactions, addition reactions and abstraction reactions. Significant solvent effects were observed. Radicals from sulfide and from hydrazine were also studied.

Studies of the kinetics of peroxy radical reactions were continued. The solvent effects on the rate constants for the reaction of the trichloromethylperoxy radical with chlorpromazine and trolox have been found to be significant and were interpreted in terms of the effect of solvent bonding and basicity. The reactivity of peroxy radicals with unsaturated compounds in several solvents was examined in order to unravel the basic mechanisms. The research is continuing

with an examination of the reactions of peroxy radicals of possible importance in the atmosphere (generated from CFCs and alternative CFCs) with several olefins to estimate the importance of these addition reactions in an olefin-rich atmosphere (such as over forests).

The database of rate constants for reactions of inorganic radicals and organic peroxy radicals in solution has been updated to cover data through the end of 1992. A major addition to this kinetic database is the inclusion for the first time of data on the reactions of carbon-centered radicals.

During the past year, rate constant studies were reported on the reactions of several organic peroxy radicals with nitric oxide. These reactions have not been reported previously and may play an important role in free radical-induced oxidative damage in the body. Of particular interest is the possibility that NO, which is produced in the endothelium, could diffuse into cholesterol-containing deposits and dramatically accelerate the oxidation rate, leading to the formation of plaque. Other processes in which these reactions should be considered include amyotrophic lateral sclerosis, reperfusion injury after ischaemia, and even aging.

## 7. 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. Many kinetic determinations, particularly for radical-radical reactions, are extracted from complex multi-component systems employing kinetic modeling programs. In such determinations, it is essential to quantify a realistic uncertainty on the measured parameters since significant systematic errors could be introduced by employing "imperfect" values for the parameters used in the modeling. Two papers were completed concerning the optimization of the experimental conditions, error analysis and the evaluation for parameters determined through complex kinetic modeling. One paper examined the self- and cross-combination reactions of HO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub> radicals which are important in atmospheric chemistry. A second paper examined the reaction kinetics of the methyl radical and the vinyl-methyl mixed radical system.

A collaboration with Dr. Louis Stief of the NASA Goddard Flight Center resulted in a determination of the rate constant for reaction of the vinyl radical with hydrogen. This process is thought to be significant in Jupiter's atmosphere and other planetary atmospheres.

## 8. Calorimetry: Experimental Determinations of Thermodynamic Properties

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

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.

Precision oxygen bomb calorimetry provides the data necessary to calculate precise and accurate enthalpies of formation which are necessary to evaluate the molecular energetics of important materials and the thermodynamic feasibility of their chemical reactions. The NIST oxygen bomb calorimetry laboratory has unique, well-characterized calorimetry equipment which is capable of making combustion measurements on samples as small as 10-15 milligrams. The capability of handling such small samples permits routine measurements on substances which are available only in small quantities, such as very high purity compounds. The laboratory also has the capability for carrying out bomb calorimetric measurements in either a static or a rotating mode. Accurate calorimetric results on organic compounds that contain sulfur, phosphorus, or halogens can be obtained only through use of a rotating bomb calorimeter.

Because of these unique facilities, the NIST oxygen bomb calorimetry laboratory is the only laboratory that is presently making precise and accurate measurements on organic phosphorus compounds. Because of the complete lack of thermodynamic data on organic compounds containing both phosphorus and sulfur, work was undertaken this year to perfect experimental methods to determine heats of combustion of such compounds. 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. In 1993, a new methodology was designed for determining the heating value of sulfur-containing cokes and coals, and four Standard Reference Materials were certified using this approach.

Data on standard molar enthalpies of formation of "high-tech" materials, which are often amorphous (glassy), can not be determined by oxygen bomb calorimetry. However, the exceptional oxidizing power of high-pressure fluorine can be brought to bear using the technique of fluorine-combustion calorimetry, thus permitting the experimental determination of the enthalpies of formation of such substances. The NIST fluorine bomb calorimetry facility, the only laboratory of its kind in the world, is working to establish, primarily by experimental methods, a database of key thermodynamic information for pure materials of importance in modern technologies. This year, calorimetric studies were successfully completed on the



following materials: crystalline  $\text{SiSe}_2$ , vitreous  $\text{SiSe}_2$ ,  $\text{S}_8(\text{AsF}_6)_2$ ,  $\text{Mo}_5\text{Si}_3$ , and several alloys in the (Zr+Fe+Al) system. The results will help elucidate the behavior of these materials under conditions used in industrial processes. Without good thermodynamic information for these materials, any long term compatibility evaluation is of little value.

An important study reported a new determination of the standard molar enthalpy of formation of liquid hydrogen fluoride at 298.15 K by direct combination of the elements in a fluorine bomb calorimeter. This study provides a key piece of data in the network of chemical thermodynamic data affecting the values assigned to thermodynamic properties of many other compounds.

In addition, during 1993 work continued on setting up and calibrating a low temperature heat capacity calorimetry laboratory to broaden the Division's capabilities to provide useful thermodynamic information to the user communities. This new facility, along with the existing bomb calorimetry laboratories, gives the NIST thermodynamics laboratories 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. The equilibrium constant is simply related to the thermochemistry of the reaction, and can be obtained if values of the enthalpy change and entropy change of the reaction are known. These quantities can, in turn, be derived from standard values of enthalpies and entropies of formation of the relevant chemical compounds taking place in the reaction. Values of entropies are usually obtained from an integration of heat capacity data over a wide range of temperature. Since Division bomb calorimetry laboratories generate data on enthalpies of formation, the NIST thermodynamics laboratories possess the ability to determine absolute values of all parameters necessary to predict chemical equilibrium constants, and will be one of only two laboratories in this hemisphere with this capacity.

## 9. Optical Detection of Reactive Intermediates

**J.W. Hudgens, R.D. Johnson III, K.K. Irikura, and J.L. Brum**

Resonance enhanced multiphoton ionization (REMPI) spectroscopy provides previously unobtainable data about the electronic structures of a wide variety of free radicals. Newly discovered REMPI spectra form the basis of new sensitive and selective schemes for the optical detection of these radicals. The technique involves tuning an intense pulsed dye laser so that the energy sum of two or three photons of laser light matches the energy of a Rydberg state of the radical of interest. Laser-excited radicals in Rydberg states then absorb an additional photon and ionize. The ionization signal is measured by detecting ions with mass spectrometry or by detecting the laser-induced electron current. REMPI detection schemes are very selective and typically give sensitivities between  $10^4 - 10^{10}$  radicals  $\text{cm}^{-3}$ .

Recent work in the REMPI laboratory continues to emphasize the development of nonintrusive, laser-based detection methods for radicals important to semiconductor materials. Because Group IIIB metal halides are volatile, they are used to transport metals to and from the surfaces during semiconductor manufacturing, and thus the species are of practical and fundamental interest. In a continuation of the series of studies of group IIIB halides of boron, aluminum, gallium, and indium halides, extensive new spectra for the short-lived aluminum and indium monochloride molecules were obtained this year.

Other studies this year included an examination of REMPI detection schemes of methyl radicals. Using REMPI spectroscopy to detect methyl radicals, scientists have studied important technological processes such as combustion, chemical vapor deposition of metallic films from organometallic precursors, catalysis, and diamond chemical vapor deposition. The new results report electronic spectra of the deuterium-labeled methyl radicals  $\text{CH}_2\text{D}$  and  $\text{CHD}_2$ . The main goals of these experiments were to acquire a more complete set of vibrational frequencies for constructing potential surfaces of the methyl radical and to obtain laser wavelengths that permit selective detection of these isotomers.

Last year, the REMPI laboratory reported the first simple, conveniently applied detection schemes for ground state methylene radicals,  $\text{CH}_2$  ( $\tilde{X}^3\text{B}_1$ ). Because  $\text{CH}_2$  plays extremely important roles in combustion and photochemistry of hydrocarbons, researchers have long wanted a sensitive optical diagnostic method. This year, a new detection method for the monofluoromethylene radical,  $\text{HCF}$  ( $X^1\text{A}'$ ) was obtained. The  $\text{HCF}$  radical is a reaction intermediate produced within fluorine-hydrocarbon flames. Halogenated ethyl radicals were also examined, and the first vibrationally-resolved optical spectrum of a substituted ethyl radical was obtained.

During the year, a study was conducted to determine the feasibility for using degenerate four-wave mixing (DFWM) technology as a remote sensing diagnostic technique for flames, plasmas, and flue gases from boilers. A project is being initiated in collaboration with scientists at Stanford University to develop a new generation of useful monitors for chemical processing. The research will concentrate upon reactive processes and chemical species of importance to industrial environments.

## 10. Kinetic Mass Spectrometry

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

This program of research in ion/molecule reaction chemistry, supported by the Department of Energy, is directed primarily at the determination and evaluation of ionic reaction mechanisms incorporating competitive reaction kinetics which may prove useful for analytical purposes. 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. Work in Division laboratories involves measurements of ion/molecule rate constants, and equilibrium constants of ion/molecule reactions as a function of temperature. The latter quantities lead to 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 1993, several collaborative projects involving the applications of ion/molecule reactions were completed. A combined experimental-theoretical study of the thermochemistry of protonation, complexation, and hydration of di- and polyfunctional ethers with Professor S. Scheiner of Southern Illinois University gave results which impact on the chemistry of biological systems (proton wires) and evaporative mass spectrometric analysis (thermo/electrospray) of polyfunctional analytes. Another experimental-theoretical study conducted with Professor C. Deakyne of Eastern Illinois University sought to determine whether carbon- or nitrogen-lone pair electrons were more effective in forming ionic hydrogen bonds; the experimental work, carried out at NIST, involved comparing results for cyanides and isocyanides. A collaboration with Professor S. El-Shall at Virginia Commonwealth University provided data derived from beam expansion experiments, as well as from NIST high pressure mass spectrometry studies, on the structures and stabilities of methanol clusters incorporating either  $\text{CH}_3\text{CN}$  or  $(\text{CH}_3)_3\text{N}$ . These two molecules were selected because they have widely differing proton affinities and form single bonds (i.e., complex clusters involving multiple bonds are unlikely). Papers describing results of all three studies have been submitted for publication.

Another accomplishment in 1993 was the observation of a gas phase protonation-decomposition sequence occurring in ethylene glycol-water mixtures in the gas phase. The reaction sequence "catalytically" converts ethylene glycol to acetaldehyde via consecutive proton transfer reactions.

Major efforts went into a re-exploration of the scale of relative proton affinities of organic molecules. 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 NIST study provided the first extensive scale with experimentally-determined entropy changes; in the past, most studies were carried out at a single temperature and estimated the entropy changes from the principles of statistical mechanics. Results from the University of Waterloo in Canada were in substantial agreement with the NIST results, but disagreed on several important details, such as the relative position in the scale of the proton affinity of isobutene. The proton affinity of isobutene has been widely used as a primary standard for assigning absolute values to the proton affinity scale. As a part of this work, an answer was found to a question which has long been a matter of speculation for organic physical chemists: the site of protonation in quinones. The results obtained in the high pressure mass spectrometer indicate that protonation occurs on the oxygen rather than at a ring site.

11. Ion Energetics and Proton Affinity Databases: The Ion Kinetics and Energetics Data Center

E.P. Hunter, S.G. Lias, S.E. Stein, J.F. Liebman (University of Maryland Baltimore County), R.D. Levin, D. Frizzell, P. Christian, and J. Reed

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: 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. Data Center publications are widely cited, collecting 437 citations in 1992, the last full year for which citation data are available.

During 1993, extensive work was carried out to produce an update to the personal computer version of the Ion Energetics Database. The Database is made up of two separate databases distributed jointly, one for positive ions and one for negative ions. An update of the Negative Ion Database was delivered to the Data Center in March by Dr. John Bartmess, who administers this database at the University of Tennessee. The update to the Positive Ion Energetics database was also completed in March, and outfitted with the powerful Structures and Properties software developed in the Division last year. This update contains 22,000 data points for 11,000 compounds, and represents a complete coverage of the literature on ionization energies and appearance energies for the time period 1971-1992. (Version 1 contained about 5,000 data points for 5,000 molecules.)

During the year, the work was initiated to update the 1984 Data Center Journal of Physical and Chemical Reference Data publication on proton affinities of molecules. The earlier publication received more citations than any other chemistry paper written in 1984. Recently, new experimental and computational work from several different laboratories (including the work in Division laboratories described above under "Kinetic Mass Spectrometry") has resulted in a considerable amount of new data, especially about entropy changes associated with proton transfer reactions. Most of the new papers compare their results to the "NIST scale", that is, to the evaluation provided in the 1984 publication. The project will include a re-evaluation of the proton affinity scale, as well as the incorporation of all data which appeared in the literature in the years 1984-1993.

12. Chemical Thermodynamics Data Evaluation - Heat Capacities and Entropies of Organic Compounds, and Estimation of Thermodynamic Properties of Organic Compounds: The Chemical Thermodynamics Data Center

E.S. Domalski

Much of the current emphasis of work in the Chemical Thermodynamics Data Center is on the evaluation of thermodynamic data for organic compounds, with the long-range goal of developing a definitive scheme for estimating thermochemical data. Such expert schemes permit the user community to readily estimate needed information for the thousands of organic compounds for which no experimental measurements have ever been made.

Experimental heat capacity data are available for a significant number of compounds. Use of estimation methods is an obvious approach to generate missing data, in particular in engineering applications. The second-order group-additivity estimation method, which has been applied so successfully by S. W. Benson and co-workers to the estimation of thermodynamic properties ( $\Delta_f H^\circ$ ,  $C_p^\circ$ ,  $S^\circ$ ) of gas phase molecules, has been extended to the condensed phase for organic compounds containing carbon, hydrogen, oxygen, nitrogen, sulfur, and halogen atoms. Work was completed this year on the derivation of second-order group parameters for the estimation of the heat capacities of organic liquids as a function of temperature, with results published in two papers in the Journal of Physical and Chemical Reference Data. Another publication which appeared in that journal in 1993 presented second-order group parameters for the estimation of enthalpies of formation, heat capacities, and entropies under standard conditions in the gas, liquid, and solid phases for many families of organic compounds including alcohols, aldehydes, ketones, ethers, organic acids, esters, heterocyclic compounds containing nitrogen, oxygen and sulfur. The estimated properties are compared with literature data for 1512 compounds. These results are also available in a person computer database, THERM/EST, available through the Standard Reference Data Program.

Other projects involve the compilation and estimation of heat capacities of organic liquids in collaboration with scientists in Europe (M. Zabransky and V. Ruzicka of the Institute of Chemical Technology, Prague; V. Majer of the Universite Blaise Pascal/CNRS, France); under the sponsorship of the IUPAC Subcommittee on Thermodynamic Data and the IUPAC Commission on Thermodynamics. A related project, the compilation entitled "Heat capacities and entropies of organic compounds in the condensed phase, Volume III" by E. S. Domalski is near completion. The work, with nearly 2000 references, includes all data from the 1984 and 1990 publications of the same title, along with the data from 1990, 1991, and 1992. The work also includes thermodynamic data for phase transitions for solid/solid, solid/liquid, and in some instances, solid/gas and liquid/gas.

A bibliography and file of papers has been compiled which contains over 1200 references to data on the thermodynamic properties of organometallic compounds. Additional references are being

collected for entry. This bibliography will serve as the basis for a project on the evaluation and estimation of the enthalpies of formation of organic silicon and boron compounds.

### **13. Chemical Database Development: The Structures and Properties Project**

**S.E. Stein, W.G. Mallard, K.K. Irikura, A.A. Levitsky (Institute of Organic Chemistry, Russia), O.V. Fateev (Russian Academy of Sciences, Russia), and D.V. Tchekhovskoi (Institute for High Temperature, Russia)**

This project is comprised of software-development work in support of many different database-development projects, both in Division data centers and other Standard Reference Data Program data centers, and (b) major data compilation projects initiated outside of regular Division Data Center activities as an off-shoot of the software development activities.

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 originally developed for use with the Ion Energetics database. A new update of the Ion Kinetics and Energetics Database was produced this year with updated software. 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, Benson-type 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, some of whom are exploring with us the possibility of adapting the programs for their own in-house use.

Work continued on the production of a database of spectroscopic properties of diatomic molecules. This database is an update of the book, "Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules" by K.P. Huber and G. Herzberg. Extensive data editing and processing was carried out and software is now being developed for release during 1994.

### **14. Data Compilation: Enthalpies of Formation of Organic Compounds**

**S.E. Stein, H.Y. Afeefy (Mansoura University, Egypt), J.F. Liebman (University of Maryland Baltimore County), R.D. Levin, D. Frizzell, P. Christian, and J. Reed**

The long-range objective of the Structures and Properties Project is to put together large databases of "structure and property" information to be used with the existing software or future updates of that software. Initially these auxiliary databases will include all the databases developed in Division data centers which are relevant, including the database of ionization energies (described under 11: Ion Energetics and Proton Affinity Databases: The Ion Kinetics and Energetics Data Center), the existing 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.

However, the most obvious type of data which is needed for a product which produces computer-generated estimations using Benson-type additivity is thermochemical data. 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 the past year, considerable progress was made on the establishment of a collection of data to serve as the basis for a new Organic Enthalpies of Formation Database. More than 6,000 papers containing data were retrieved from the literature and abstracted, and data on 5,500 compounds were reviewed and entered into the database. It is anticipated that the preliminary version of the database, planned for release as a personal-computer product about a year from now, will contain data on well over 8,000 compounds from more than 10,000 scientific publications. When completed, the database will be released for use with the Structures and Properties software. After evaluation of the data, a hard copy publication will also be produced.

This data collection, when completed, will provide a single, integrated database resource for the Thermochemistry Estimation project being organized as a collaboration of the Chemical Thermodynamics Data Center.

#### 15. The NIST/EPA/NIH Mass Spectrometry Data Center

**S.E. Stein, P.J. Ausloos, C.L. Clifton, S.G. Lias, O.V. Fateev (Russian Academy of Sciences, Russia), A.A. Levitsky (Institute of Organic Chemistry, Russia), and A.I. Mikaya (Topchiev Institute of Petrochemical Synthesis, Russia)**

This Data Center was created in October, 1988, for the purpose of maintaining, updating, and improving the NIST/EPA/NIH Mass Spectral Database. The computerized collection of electron mass spectra was originally put together at EPA and NIH, and starting in 1978, was distributed by the Standard Reference Data program while still being maintained by the EPA. In late 1988, the primary responsibility for the maintenance, evaluation and updating of the database was moved to NIST from EPA. Since then, four updates of the database have been released. The database is distributed through the Standard Reference Data Program to instrument manufacturers who include the database in 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.

No new update of the database was planned for 1993. Efforts this year have concentrated on (1) continuing the systematic evaluation of all the spectra in the collection; (2) continuing to acquire new spectra through in-house determinations and through purchases or donations of spectra from other laboratories, notably at the National Institutes of Health; (3) continuation of work on production of Windows and MacIntosh versions of the database; (4) development of code to allow porting of the mass spectral database to other computer environments (particularly useful for instrument companies); (5) systematic studies and developmental work on mass spectral search algorithms.

This year's evaluation task was considerably more difficult than earlier work, which involved comparing replicate spectra or spectra of similar compounds. In 1993, the remaining work to be done on evaluating the database involved examining individual spectra - spectra for which the evaluator has nothing to compare against, and therefore must make use only of first principles.

Numerous problems and errors have been uncovered and the problem spectra have been deleted from the collection, or appropriate corrections have been made. The increase in quality of the NIST/EPA/NIH Mass Spectral Database as a result of the systematic evaluation effort has been widely noticed by the user community.

Considerable attention has been given this year to developing and evaluating improved software for matching spectra of unknown compounds against mass spectral databases. A detailed statistical analysis of the performance of the NIST search software as compared to other search systems in common use has been carried out, and results presented in talks at the American Chemical Society Meeting and at the Pittsburgh Conference.

During the year, work was completed on the development of a new distribution format for the database provided to distributors. In the past, distributors have received a simple ASCII file on tape or CD-ROM, without software for searching or manipulating the data. The distributors have had to re-format the database for incorporation into their own systems, and have provided their own search software. Starting in 1994, the new format (a so-called dynamic link library) will permit the distributors to access a package, including the database and all of the NIST-developed software for searching and manipulating the data, without having to do any re-formatting or programming. This will effect a large savings in time and effort for the distributors of the database.

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.



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

1. **Publications**

Alfassi, Z.B., Padmaja, S., Neta, P., and Huie, R.E., "Solvent Effects on the Rate of Reaction of  $\text{Cl}_2^-$  and  $\text{SO}_4^-$  Radicals with Unsaturated Alcohols," *Int. J. Chem.* in. 25, 151 (1993).

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## 2. Talks

- Brum, J.L., "Electronic Spectrum of CH<sub>2</sub>D and CDH<sub>2</sub> Radicals Via REMPI Spectroscopy," National American Chemical Society Meeting, Denver, CO, March 31, 1993.
- Domalski, E.S. and E.D. Hearing, "THERM/EST - Electronic Database and Interactive Program to Estimate the Thermodynamic Properties of Organic Compounds at 298.15 K," 48th Annual Calorimetry Conference, Duke University, Durham, NC, July 18, 1993.
- Domalski, E.S., "Monitoring and Optimizing the Incineration of MSW," Czechoslovak-French-Polish Conference on Calorimetry and Thermodynamics with Application to Contemporary Problems," Institute of Chemical Technology, Prague, Czech Republic, September 4, 1993. Invited
- Fahr, A., "Error Analysis For Complex Kinetics Systems, Methyl-Vinyl Cross Radical Reactions," Third International Conference on Chemical Kinetics, Gaithersburg, MD, July 13, 1993.
- Fahr, A., "Photolysis of Methyl Vinyl Ketone at 193.3 nm," Third International Conference on Chemical Kinetics, Gaithersburg, MD, July 15, 1993.
- Hudgens, J. W., "New Rydberg States of Gas-Phase Aluminum Halides Observed by Resonance-Enhanced Multiphoton Ionization Spectroscopy," National American Chemical Society Meeting, Denver, CO, March 31, 1993.
- Hudgens, J. W., "New Ways to Optically Detect CH<sub>2</sub> and HCF Radicals using Resonance-Enhanced Multiphoton Ionization Spectroscopy," International Society of Optical Engineering, Los Angeles, CA, January 21, 1993. Invited
- Hudgens, J.W., "Mass Spectroscopic Studies of Radicals of Interest to Semiconductor Processing Using REMPI," University of Texas at Austin, TX, April, 26, 1993. Invited
- Huie, R.E., "The Chemistry of NO<sub>2</sub>· and Some of Its Reactions," Chemical Kinetics and Thermodynamics Division, Gaithersburg, MD, December 2, 1992.
- Huie, R.E., "Reactions of Haloperoxy Radicals in Various Solvents. Implication for the Atmosphere Reactions of the Radicals," Science and Technology for Environmental Protection / Alternate Fluorocarbons Environmental Acceptability Study Workshop on the Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere, Dublin, Ireland, March 23, 1993. Invited
- Huie, R.E., "Reactions of NO with ·O<sub>2</sub><sup>-</sup> and RO<sub>2</sub>·," Third International Conference on Chemical Kinetics, Gaithersburg, MD, July 14, 1993.

- Irikura, K., "Energetics of Third-Row Transition Metal Carbene Ions  $MCH_2^+$ ," 8th American Conference on Theoretical Chemistry, Rochester, NY, June, 28, 1993.
- Irikura, K., "Multiphoton Spectroscopy of Pseudo-Ions," University of Virginia, Charlottesville, VA, February 10, 1993. Invited
- Irikura, K., "Multiphoton Ionization Spectroscopy of  $CH_2$  and CHF," National American Chemical Society Meeting, Denver, CO, March 31, 1993.
- Irikura, K., "Multiphoton Spectroscopy of Singlet Carbenes: HCF and DCF," 48th International Symposium on Molecular Spectroscopy, Ohio State University, Columbus, OH, June 16, 1993.
- Irikura, K., "Spectroscopy of Pseudo-Ions: Rydberg-State-Resonant Multiphoton Ionization," Gordon Research Conference, Ventura, CA, March 3, 1993.
- Irikura, K., "Carbene Detection by Resonant Photoionization," Third International Conference on Chemical Kinetics, Gaithersburg, MD, July 12, 1993.
- Irikura, K., "Thermochemistry of Sulfur Fluorides," Third International Conference of Chemical Kinetics, Gaithersburg, MD, July 13, 1993.
- Johnson, R.D., "Electronic Spectra of AlCl, GaCl and InCl," 48th International Symposium on Molecular Spectroscopy, Ohio State University, Columbus, OH, June 16, 1993.
- Johnson, R.D., "Spectra of GaCl and InCl by REMPI Spectroscopy," National American Chemical Society Meeting, Denver, CO, March 31, 1993.
- Johnson, R.D., "Group IIIB Monohalide Detection by REMPI Spectroscopy," Third International Conference on Chemical Kinetics, Gaithersburg, MD, July 12, 1993.
- Johnson, R.D., "Thermodynamics and Detection of Transient Species Using REMPI Spectroscopy," SEMATECH Workshop, NIST, Gaithersburg, MD, October 1, 1992.
- Kirklin, D.R., "Enthalpy of Combustion of Triphenylphosphine Sulfide," Seventh International Simulant Workshop, Aberdeen Proving Grounds, MD, March 3, 1993.
- Kirklin, D.R., "Enthalpy of Combustion of Triphenylphosphine Sulfide," 48th Annual Calorimetry Conference, Duke University, Durham, NC, July 21, 1993.
- Kirklin, D.R., "Estimation Methods for Organic Phosphorus Compounds," 20th Annual Meeting of the National Organization of Black Chemists and Chemical Engineers, Indianapolis, IN, April, 13, 1993. Invited

- Kurylo, M.J., "The Latest Scientific Findings on Stratospheric Ozone Depletion and Its Effects on Ground Level Ultraviolet Radiation," Keynote Address at the Annual Meeting of the Sun Glass Association of America, Kona, HI, October 20, 1992. Invited
- Kurylo, M.J., "Complementary Research Opportunities under the Network for the Detection of Stratospheric Change (NDSC)," Japanese NDSC Workshop, National Institute for Environmental Studies, Tsukuba, Japan, November 19, 1992. Invited
- Kurylo, M.J., "The Ozone Layer," Asia-Pacific International Space Year Conference, Tokyo, Japan, November 17, 1992. Invited
- Kurylo, M.J., "The U.S. Research Program in Stratospheric Chemistry," Polar Stratospheric Ozone Workshop, Asia-Pacific International Space Year Conference, Tokyo, Japan, November 18, 1992. Invited
- Kurylo, M.J., "Stratospheric Ozone and Related Research Activities Conducted by the U.S. Government and Industry," UNEP/WMO Research Managers Meeting on Research Related to the Health and Environmental Effects of Ozone Modification, Geneva, Switzerland, March 11, 1993. Invited
- Kurylo, M.J., "Gas Phase Reaction Rate Studies and Gas and Liquid Phase Absorption Cross Section Measurements for CFC Alternatives," Science and Technology for Environmental Protection / Alternate Fluorocarbons Environmental Acceptability Study Workshop on the Kinetics and Mechanisms for the Reactions of Halogenated Organic Compounds in the Troposphere, Dublin, Ireland, March 23, 1993. Invited
- Kurylo, M.J., "The Atmospheric Chemistry of Methyl Bromide: How Well Can We Determine Its Atmospheric Lifetime and Quantify Its Anthropogenic Source?," US. Environmental Protection Agency Public Hearing on the Proposal to Regulate Methyl Bromide, Washington, DC, April 8, 1993. Invited
- Kurylo, M.J., "An Overview of NASA's Research and Analysis Programs in Atmospheric Chemistry," National Academy of Sciences / Committee on Atmospheric Chemistry Meeting on U.S. Government Research, Washington, DC, April 14, 1993. Invited
- Kurylo, M.J., "Tropospheric and Stratospheric Research," NASA Mission to Planet Earth Research and Analysis Review Panel Meeting, Washington, DC, June 15, 1993. Invited
- Neta, P., "Electrophilic Properties of Radicals. Reaction Rates and Solvent Effects," Miller Conference on Radiation Chemistry, Windermere, England, April 5, 1993. Invited
- Neta, P., "Solvent Effects on Rate Constants of Free Radical Reactions," Radiation Research Society Meeting, Dallas, TX, March 23, 1993. Invited



- Neta, P., "Solvent Effects on the Rate Constants for Electron Transfer Reactions of Peroxyl Radicals," 17th DOE Solar Photochemistry Research Conference, Brainerd, MN, June 8, 1993. Invited
- O'Hare, P.A.G., "Thermochemistry of Some Silicon-Containing Inorganic Compounds," 13th Experimental Thermodynamics Conference, Bristol, United Kingdom, March 25, 1993. Invited
- Stein, S., "Computer-Assisted Method for Improving the Quality of a Mass Spectral Database," Pittsburgh Conference, Atlanta, GA, March 8, 1993.
- Stein, S., "The NIST IR Database Program," IR Workshop in Eastern States Analytical Symposium, Somerset, NJ, November 18, 1992. Invited
- Stein, S., "Quality Control in a Comprehensive Mass Spectral Database," 41st American Society for Mass Spectrometry Conference on Mass Spectrometry and Allied Topics, San Francisco, CA, May 30, 1993.
- Stein, S., "Chemical Database Development at NIST," Eastman Kodak Company, Rochester, NY, June 21, 1993. Invited
- Stein, S., "Comparative Study of Mass Spectral Search Algorithms," American Chemical Society Symposium on "Spectroscopic Databases: Computer Innovations for Search and Interpretation," Chicago, IL, August 24, 1993. Invited
- Tomaszkiewicz, I., "The Standard Molar Enthalpies of Formation of the Crystalline and Vitreous Forms of Silicon Diselenide by Fluorine Combustion Calorimetry," 48th Annual Calorimetry Conference, Durham, NC, July 20, 1993.
- Tsang, W., "Chemical Kinetics of Fire Suppression," Ballistic Research Laboratory, Aberdeen, MD, December 15, 1992. Invited
- Tsang, W., "Hydrogen Atom Induced Decomposition of Trichloroethylene at High Temperatures," American Institute of Chemical Engineers, Miami Beach, FL, November 2, 1992.
- Tsang, W., "Chemical Kinetics Data Base of Hydrocarbon Combustion," Fifteenth Combustion Research Conference, Lake Harmony, PA, June 2, 1993.
- Tsang, W., "Single Pulse Shock Tube Study on the Thermal Decomposition of 3,3,4,4-Tetramethylhexane and the Stability of t-Amyl Radical," Third International Conference on Chemical Kinetics, Gaithersburg, MD, July 12, 1993.

Tsang, W., "Single Pulse Shock Tube Studies on the Reactions of Hydrogen Atoms with Acetone and Dimethyl Ether," 19th International Symposium on Shock Waves, Marseilles, France, July 27, 1993.

Tsang, W., "Status Report - Kinetic Database for Propellant Combustion," Joint Army, Navy and Air Force (JANAF) Combustion Meeting, Hampton, VA, October 19, 1992.

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

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

4. **Patent Awards and Applications**

None

5. **SRM Activities**

SRM 2692a Calorific Value and Sulfur in Coal (Certified)  
SRM 2775 Calorific Value and Sulfur in Coke (Certified)  
SRM 2682a Calorific Value and Sulfur in Coal (Updated)  
SRM 2685a Calorific Value and Sulfur in Coal (Updated)

6. **SRD Activities**

NIST Chemical Kinetics Database (update)  
DIPPR Project 861, Aqueous Electrolyte Solution Database (new)  
NDRL/NIST Liquid Phase Kinetics Database (new)  
Positive and Negative Ion Energetics (update)  
Structure and Properties (update)  
THERM/EST (update)

7. **Calibrations**

None

## 8. Committee Assignments

### **E.S. Domalski**

The Calorimetry Conference (Chairman-Elect and Program Chairman)  
ASME Research Committee on Industrial and Municipal Wastes  
IUPAC Subcommittee on Thermodynamic Data (Secretary)

### **R.F. Hampson**

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

### **J.T. Herron**

Organizing Committee, Third International Conference on Chemical Kinetics  
IUPAC Commission on Chemical Kinetics (Chairman)  
IUPAC Subcommittee on Data for Low Pressure Plasma Chemistry  
JANNAF Panel on Kinetic and Related Aspects of Propellant Chemistry  
Washington Editorial Review Board

### **J.W. Hudgens**

NIST Chemical Science and Technology Laboratory Colloquium Committee  
Organizing Committee and Co-chair for the Symposium on Laser Techniques for  
State-Selected and State-to-State Chemistry 94/SPIE, Los Angeles, CA

### **R.E. Huie**

Poster Session Committee - CHEMRAWN VII  
Environmental Protection Agency Grant Review Panel  
American Working Group in Physical and Material Sciences of the Indo-US  
Subcommission on Science and Technology  
Organizing Committee, Third International Conference on Chemical Kinetics  
(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)  
Editorial Advisory Board, International Journal of Chemical Kinetics  
Advisory Panel, NASA Atmospheric Effects of Aviation Project

**S.G. Lias**

ASTM E-49 Committee on Computerization of Material Property and Chemical Data  
Joint Committee on Atomic and Molecular Physical Data  
American Society for Mass Spectrometry, Measurements and Standards Committee  
NIST Diversity Council  
American Society for Mass Spectrometry, Nominating Committee

**W.G. Mallard**

ASTM E-49 Committee on Computerization of Material Property and Chemical Data  
Steering Committee for the NIST/EPA/NIH Spectral Database

**D. Neumann**

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

**P.A.G. O'Hare**

International Scientific Organizing Committee, IUPAC Conference on Chemical Thermodynamics, Clermont-Ferrand, France, 1994  
IUPAC Commission on Thermodynamics (Chairman)

**S.E. Stein**

Air Pollution Modeling Instrumentation and Measurement Methodology Group.  
Alternate Councilor, Computers in Chemistry Division, American Chemical Society

**W. Tsang**

JANNAF Panel on Kinetic and Related Aspects of Propellant Chemistry  
Review Committee, 24th International Symposium on Combustion  
Organizing Committee, Third International Conference on Chemical Kinetics

**9. Editorships**

**M.J. Kurylo**

International Journal of Chemical Kinetics (Editorial Board)

**S.G. Lias**

Organic SEARCH (Structure, Energies and Reactivity in Chemistry) Series (Chapman and Hall)

**P. Neta**

Radiation Physics and Chemistry (Regional 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 8, 1992**

Dr. Richard Carter, Oak Ridge National Laboratory, Oak Ridge, TN, "Thermodynamic Properties of Aqueous Electrolyte Solutions at High Temperatures and Pressures." (Division Sponsor: D. Archer)

**January 14, 1993**

J.A. Martinho-Simões, Instituto Superior Técnico, Lisbon, Portugal, "Energetics of Zr and Nb Organometallic Compounds." (Division Sponsor: J. Liebman)

**January 15, 1993**

Mark Bausch, Southern Illinois University, Carbondale, IL, "Investigations of the Stabilities and Reactivities of Carbon and Nitrogen Centered Ions, Radicals and Radical Ions." (Division Sponsor: J. Liebman)

**January 29, 1993**

Dr. A. Harriman, University of Texas, Austin, TX, "Electron Tunneling in DNA (Ultrafast Laser Spectroscopy Studies)." (Division Sponsor: P. Neta)

**February 23, 1993**

Professor W. R. Dolbier, Department of Chemistry, University of Florida, Gainesville, FL, "Unimolecular Reactions of Fluorinated Hydrocarbons." (Division Sponsor: S. Stein)

**March 3, 1993**

Eric J. Cotts, Department of Physics & Center for Materials Research, Binghamton, NJ, "Calorimetric Study of the Chemical Kinetics and Energetics of Solid State Reactions in Metal Diffusion Couples." (Division Sponsor: E. S. Domalski)

**March 12, 1993**

Jeffrey Manion, SRI International, Menlo Park, CA, "Destruction of Unsaturated Chlorinated Organics at High Temperature." (Division Sponsor: W. Tsang)

**March 16, 1993**

Vladimir G. Zaikin, Institute of Petrochemical Synthesis, Moscow, Russia, "Reaction Gas Chromatography / Mass Spectrometry: Principles and Application." (Division Sponsor: P. Ausloos)

**March 19, 1993**

Dr. Steen Steenken, Max Planck Institute for Radiation Chemistry, Mulheim, Germany, "Conversion of Carbenes into Carbenium Ions by Alcohols: Mechanistic Studies Using Laser Flash Photolysis." (Division Sponsor: P. Neta)

**March 26, 1993**

J. Bruce Schilling, Amoco Corporation, Naperville, IL, "Industrial Applications of Mass Spectrometry." (Division Sponsor: J. Herron)

**May 20, 1993**

Dr. David Green, Department of Chemistry, Stanford University, Stanford, CA, "Laser-based Remote Sensing for Plasma Diagnostics." (Division Sponsor: J. Hudgens)

**June 28, 1993**

Prof. S.H. Bauer, Department of Chemistry, Cornell University, Ithaca, NY, "Condensation Flu and Estimates for Super Saturated Vapors According to Kinetic and Molecular Models." (Division Sponsor: W. Tsang)

**July 7, 1993**

David Sparkman, Product Manager GC/MS, Varian Chromatography Systems, Walnut Creek, CA, "Applications of Reference Data in Mass Spectrometer Data Systems." (Division Sponsor: S. Stein)

**July 7, 1993**

Jai P. Mittal, Bhabha Atomic Research Center, Trombay, Bombay, India, "Pulse Radiolysis Studies on Hydroxyquinones." (Division Sponsor: P. Neta)

**July 23, 1993**

P. Mulder, Leiden, University, The Netherlands "Bond Dissociation Energies in Functionalized Aromatics." (Division Sponsor: R. Huie)

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

**May 19-20, 1993**

"Industrial Applications of Computational Chemistry," National Institute of Standards and Technology, Gaithersburg, MD (W. Tsang and M. Zachariah, 836).

**July 12-17, 1993**

"Third International Conference on Chemical Kinetics: Reactions in Gas and Condensed Media," National Institute of Standards and Technology, Gaithersburg, MD (R.E. Huie).

**August 24, 1993**

American Chemical Society Symposium on "Spectroscopic Databases: Computer Innovations for Search and Interpretation," Chicago, Illinois (S.G. Lias)

**12. Cooperative Research Agreements and IPA**

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

Professor Eric J. Cotts, Dept. of Physics and Center for Materials Research, State University of New York at Binghamton (IPA)

### III. Inorganic Analytical Research Division (834)

James R. DeVoe, Chief  
William F. Koch, Deputy Chief

#### A. Division Overview

The Inorganic Analytical Research Division (IARD) conducts research and development on the accurate quantitative measurement of the inorganic chemical composition of materials. These efforts in chemical metrology include the development and deployment of advanced analytical methods, instrumentation, and reference materials. Our research delves into the fundamental and underlying principles of the chemical processes and reactions involved in chemical analyses in order to adapt, improve, and advance the science of analytical chemistry to meet the ever changing and always demanding needs of U.S. industry. The Division is aligned according to discipline and consists of four groups: Atomic and Molecular Spectrometry, Electroanalytical Research, Mass Spectrometry, and Nuclear Methods.

IARD remains responsive to the needs of its constituencies through numerous type of interactions and outputs. Complementing our permanent staff of 43 scientists and engineers, 41 guest scientists conducted research and made measurements in our laboratories, 13 from industry, 18 from universities, and 10 from other government agencies. In addition, we continue to provide specialized chemical analyses for other organizations both within and outside of NIST. In most cases, these analyses are for establishing a benchmark measurement for a specific type of material for an industrial or government laboratory. For example, this past year we analyzed a series of reference material fuel oils for uranium and thorium. These materials are being used as a reference calibrator by the Environmental Protection Agency for evaluating the emission of these elements in electric power plants. In FY93, the Division issued 390 Reports of Analysis and Calibration, primarily in keeping with our strong commitment to the certification of Standard Reference Materials. These reports covered over 90 Standard Reference Materials for 18 elements. This past year we have spent considerable effort to conform to the new NIST 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.

Created in 1990 within the Inorganic Analytical Research Division as a pioneering effort to provide the roadmap for the automation of analytical chemistry, the Consortium for Automated Analytical Laboratory Systems (CAALS) has systematically and purposefully shifted its focus from inorganic analysis (after successfully demonstrating its application in microwave-assisted dissolutions) to organic analyses. Consequently, the administration of the Consortium was transferred to the Organic Analytical Research Division, effective October 1, 1993. During fiscal year 1993 (FY93) excellent progress was made in producing the first standards-in-communication



protocol between the various components that make up an analytical system. CAALS will work with the Department of Energy (DoE), which is a charter member of the consortium, to promulgate this standard via their planned automation programs. In addition, we have enlisted the assistance of several post doctoral appointees to write software that will implement this standard on computer platforms often used in industry.

A summary of some of the outstanding activities of the four Groups follows, with expansion of the major accomplishments provided in the Technical Highlights.

Nuclear Methods Group. 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, supported in part by NIST competence funding, made significant progress in the deployment of advanced instrumentation. In collaboration with X-ray Optical Systems, Inc. (a recipient of a NIST Advanced Technology Program, ATP award) and the Kurchatov Institute in Moscow, a major breakthrough in neutron focussing, via a glass capillary, was realized. The combination of our invention of a spatially sensitive real-time neutron detector with their invention of the fabrication of a glass fiber lens resulted in a spot size of less than 0.5 mm with a gain of over a factor of twenty in neutron fluence.

The Prompt Gamma Activation Analysis (PGAA) facility in the CNRF has been significantly upgraded by making the entire sample/detector region vacuum tight and helium purgable, and by installing a Compton scatter anti-coincidence radiation detection system to reduce background radiation. These improvements now permit accurate measurements of low levels of a number of elements, including hydrogen, a difficult element to determine by any method. This technique was recently applied to the analysis of turbine blades. 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 PGAA indicated an elevated hydrogen concentration in the regions of failure. A recent curious twist has been observed in the measurement of highly scattering samples such as those with a large number of protons. If the sample is at room temperature, the cold neutrons become heated with a subsequent decrease in activation cross section.

For Neutron Depth Profiling (NDP), a new highly versatile 60-cm diameter chamber has been designed for ultra-high vacuum capability. The instrument's improved sensitivity resulted in the measurement of the depth of boron distribution in diamond films which are being considered as a new semiconductor material. Time-of-flight instrumentation has been developed and preliminary measurements have been made of near surface nitrogen in calibration materials. We plan to incorporate time-of-flight measurements in this instrument for the purpose of improving the depth resolution. By measuring the heavy residual nucleus of a light element such as nitrogen, it may be possible to measure distributions of depth to a maximum of ten nanometers with a resolution of a fraction of a nanometer.

Significant accomplishments have been made in compositional metrology in the Nuclear Method Group. An important paper was published on the trace element composition of marine mammal livers which was done in collaboration with NOAA and EPA who support the Specimen Bank. A four year international study in collaboration with the IAEA involving the measurement of trace elements in foodstuffs was completed this year. The group serves a special function among the laboratories of the world performing neutron activation analysis by conducting inter-laboratory comparisons of trace element concentrations in botanical and biological materials, and recently, we have initiated a study of the trace element measurements in silicon. In our ongoing automation efforts, we have installed a versatile robot to transfer samples from a shielded reservoir to a radiation detector. The robot has the capability of handling many types of containers and position them precisely near the detector.

Mass Spectrometry Group. The potential for high accuracy measurement in the Mass Spectrometry Group rests on the high precision with which isotope abundance ratios can be measured. This precision ranges from a few tens of parts per million when using thermal ionization with electromagnetic focussing to a few parts per thousand when using an inductively coupled plasma source with quadruple focussing mass spectrometric detection (ICP-MS). Recently, the Group has emphasized the use of ICP-MS in the certification of Standard Reference Materials (SRMs) because of its experience over the past three years in evaluating and improving the performance of the NIST instrumentation. Savings in time without sacrificing accuracy can be realized in some selected cases by performing multiple isotope spiking.

The Group continues in its commitment to improving the accuracy of the atomic weights of the naturally occurring elements. The current effort is on zinc which will be our 17th element. Zinc has one of the least well known atomic weights in the periodic table, and we are striving to improve its accuracy by a factor of ten. Element assay and purification procedures have been completed, preliminary to the determination of the atomic weight of zinc. A few experiments have been completed this past summer to determine appropriate operational parameters for the mass spectrometric measurements. It is expected that a least one year will be required to establish the requisite precision for these measurements. In addition to the importance of having accurately known atomic weights, this project provides the Group with the opportunity to develop and hone the necessary expertise to perform analyses of the highest accuracy possible.

Over the last few years, the Group has gradually been phasing out of the business of designing and fabricating mass spectrometers at NIST. Commercially available mass spectrometers now come close to matching the capabilities of the instruments designed in this Group over the last 25 years. Only national metrology laboratories require the high accuracies that the NIST instruments can provide. At the beginning of FY93, we had only enough parts to assemble two additional spectrometers. We are in the process of completing the installation of one of these at the Centre Bureau for Nuclear Measurements (now known as the Institute for Reference Materials and Measurements (IRMM), Geel, Belgium.

This year the College of American Pathologists (CAP) expanded its Reference Laboratory for Clinical Analysis, established within the Organic Analytical Research Division (OARD) over a decade ago, to include inorganic analysis. This program, formalized by a CRADA between CAP and NIST, now supports three Research Associates (two in OARD and one in IARD). The focus of this effort is to develop 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. This program is an ideal match to our primary mission, and provides the much needed accuracy base to the analyses vital to the medical community.

The Group has been a pivotal player in an international program sponsored by the International Bureau of Weights and Measures (BIPM) to establish measurement accuracy using isotope dilution mass spectrometry, considered to be one of the most accurate quantitative analytical methods. This year's program involved the measurement of two sets of aqueous solutions containing three elements each. Successful completion of this international study should form the foundation for international comparability of quantitative chemical analysis.

Atomic and Molecular Spectrometry Group. An important new activity in the Atomic and Molecular Spectrometry Group is the incorporation of flow injection techniques prior to instrumental analysis. The goal is to automate some of the chemical separations and sample preparation procedures in an on-line manner, and consistent with the CAALS modular approach. This past year, methods have been developed using hydride volatilization separation for the analysis of As and Se in conjunction with atomic absorption quantitation. This new approach furnished certification quality data for 6 different SRMs this year.

The Fourier transform UV/VIS spectrometer is being used in collaboration with Iowa State University to generate an ICP-OES wavelength reference atlas. For this project, a high current hollow cathode lamp was constructed to improve the FT calibration accuracy, extensive studies were made of calibration accuracy and transfer, and upgrades were made to the instrument and the plasma for the final phase of the work. Continuing studies on the measurement of glow discharge spectra resulted in one publication on noise considerations, and line profile studies in the ICP and glow discharge were directed to the study of systematic trends in pressure broadening and shifts, and in Doppler broadening.

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 program with the Consortium on Process Analytical Chemistry (CPAC) to help establish a means to transfer calibration functions on a multivariate basis among laboratory based spectrometers. The ultimate goal is to be able to provide field analyzers with a common calibration function. Preliminary studies have established criteria for specifying the types of optical materials which are needed as well as the required measurement accuracy for wavelength and transmittance density. In conjunction with the continuing effort to improve optical absorbance measurements in the visible and ultra-violet, a new charge coupled device camera is being employed to characterize optical material homogeneity.

Laser enhanced ionization (LEI) spectroscopy was originally developed in our laboratory and has been successfully applied to ultra-trace determinations of elements using electrical current detection methods. We have recently coupled mass spectrometric (MS) detection with LEI to demonstrate ionization enhancements in both the inductively coupled plasma (ICP) and the chemical flame. These experiments provide an independent means to map the sampled regions of the plasma and to define ion beam transit times in the ICP-MS. Further studies will be directed toward improving the selectivity of LEI analyses using this mode of detection.

A procedure has been developed for characterizing solid conductive sample homogeneity over several square centimeters with millimeter resolution. The system uses a glow discharge optical emission source coupled to a Hadamard Spectrometer. The source for analyzing metals has been designed and fabricated, and the required Hadamard masks have been fabricated and tested. Multiple millimeter sized discharges have been maintained on a metal substrate using this system. Data for preliminary test samples have proven in principle that compositional mapping can be accomplished with 4-mm resolution over a total area of 2X2 cm. Optimized transfer and integrating optics are now being designed.

At the request of the Standard Reference Materials Program and the Environmental Protection Agency, we have begun a program to evaluate selectively certain leaching methods on certain SRMs. Such a program requires careful design of the methods and appropriate testing to determine their constancy with time. The first efforts at characterizing the EPA 3050 leach method have been completed. A factorial designed experiment varies 7 variables at two levels to identify the parameters which must be carefully specified and controlled to maximize the recovery of lead in paint samples. This approach will be extended to examine other leach methods for lead in soils and dust.

Electroanalytical Research Group. The Electroanalytical Research Group, continuing its research in the development of much-needed standards for electrolytic conductivity measurements, has developed a new low electrolytic conductivity reference material that can be used to calibrate water purity in power plants. The latest standards are in the range of 5 to 30  $\mu\text{S}/\text{cm}$  and consist of benzoic acid and potassium chloride in a 30% propanol-water mixture. 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. This past year it has been used for the verification of the purity of potassium dichromate, potassium chloride, and lithium carbonate. 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 Directions. The Division intends to emphasize 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 the emerging technologies. We will continue to provide the chemical measurement infrastructure for the nation. Responding to the realities of the global marketplace, we will expand our international collaborations and intercomparisons. Although CAALS is now administratively removed from IARD, the Division will continue its support of the objectives and goals of this important project, and will implement the CAALS principles of automation in its method and instrument development activities.

**B. Selected Technical Reports  
(Inorganic Analytical Research Division)**

**1. Selective Laser-induced Ionization in an ICP-MS**

**G.C. Turk, Lijian Yu (University of Missouri), and S. Roy Koirtyohann**

Isobaric interference from polyatomic species is probably the most significant problem encountered in ICP Mass Spectrometry, and a variety of techniques for the reduction of these interferences are being explored by many researchers. We have joined this effort with the idea of increasing the selectivity of the measurement through a combination of mass spectrometry and optical spectroscopy. The approach uses laser spectroscopy to selectively ionize neutral atoms in the ICP with subsequent detection of the laser-produced ions by quadrupole mass spectrometry.

We have selectively ionized strontium atoms in an ICP by both laser-enhanced ionization (LEI) and resonance ionization spectroscopy (RIS), with mass spectrometric detection. The experiment was carried out with a modified commercial ICP-MS capable of synchronized gated detection of the ion pulses generated by excimer pumped dye lasers.

The greatest limitation encountered was the high degree of non-laser ionization in the ICP. Even under conditions chosen to maximize the population of neutral analyte atoms in the ICP, most of the analyte is directly ionized by the ICP alone, without the aid of laser excitation. For this reason, we have replaced the ICP with a source which provides a high neutral atom fraction and very low background ionization, namely a hydrogen flame. The ionization count rate observed for Na in an Ar-O<sub>2</sub>-H<sub>2</sub> flame following the pulsing of dye lasers tuned to Na transition wavelengths, is approximately 1000 times greater than the natural thermal ionization of Na in the flame. The delay and duration of the LEI signal is determined by the transport time from the laser excited regions of the flame, into and through the mass spectrometer.

By contrast, an enhancement of only 10% over the level of natural ionization was observed in the ICP using LEI. The pulse duration in the ICP was only 0.2 ms (FWHM), due to the high rate of ion-electron recombination which prevents laser-produced ions from much of the laser-excited volume from reaching the mass spectrometer interface.

**2. The Preparation and Certification of a Fluoride Anion Standard Solution**

**C.M. Beck II and T.A. Butler**

Fluoride anion standard solutions are commonly made from high-purity sodium fluoride. The assay is determined by the stoichiometry, atomic weights and gravimetric data and checked by ion-chromatographic comparison to an independently prepared fluoride standard. We recently

developed an independent method to assay the fluoride in SRM 3183 (Fluoride Anion Solution Standard) using high-precision titrimetry. This new method avoids the assumption that the fluoride salt is pure. The potential danger of trusting the purity of a salt was pointed out a century ago, by T. W. Richards (who won the 1914 Nobel Prize in chemistry for his accurate determination of atomic weights by chemical methods). He warned of included and occluded water and other impurities in even the most carefully purified salts.

In order to verify the concentration of fluoride in SRM 3183, the bulk solution was assayed for fluoride before bottling by titration with standardized lanthanum solution of suitable concentration. The reaction for the titration is  $\text{La}^{+3} + 3\text{F}^- \rightarrow \text{LaF}_3 \downarrow$ . The endpoint is detected potentiometrically using a fluoride electrode. SRM 3127a (Lanthanum Spectrometric Solution Standard) was used to standardize the lanthanum titrant by EDTA titrimetry. The lanthanum assay of SRM 3127a had been established by a high-accuracy comparison by EDTA titrimetry to high-purity lanthanum metal from Ames Laboratory. The Ames lanthanum metal has been analyzed for every element and the total impurities amount to less than 100 ppm.

For the fluoride assay of SRM 3183, three 50-mL aliquots of the solution were pipetted into each of three Teflon beakers using a carefully calibrated pipet. The laboratory temperature was recorded, because all values had to be converted to a weight-weight basis since SRM 3183 is certified in mg/Kg. Each aliquot was then titrated with the standardized lanthanum solution using a fluoride-calomel electrode pair for endpoint detection. The bulk of the titrant was added until the solution was near the endpoint. The titrant was then added in 0.10-mL increments and the millivolt reading recorded for each increment. The volume corresponding to the inflection point (assumed to be very close to the true endpoint) was determined from the zero crossing point of the calculated second derivative of the titration curve. The overall uncertainty in the analyte value was calculated from the propagation of the errors associated with the preparation of the high-purity lanthanum metal solution (SRM 3127a), the comparison of SRM 3127a to the lanthanum titrant solution, and the comparison of the fluoride assay of SRM 3183 to the lanthanum titrant using potentiometric titrimetry. The fluoride concentration in the SRM was determined to be one part per thousand more than that calculated by the gravimetric data.

### 3. The Development of a System for Glow Discharge Atomic Emission Imaging of Solid Surfaces

M.R. Winchester and M.L. Salit

Metal SRM candidate materials must be assessed for elemental concentration homogeneity over dimensions as large as several centimeters prior to SRM certification. This has traditionally been accomplished at NIST with spark source Optical Emission Spectroscopy (OES) and X-Ray Fluorescence Spectroscopy (XRF). Recently, we have begun developing a system based on a novel glow discharge (GD) atomic emission device as a total approach to homogeneity assessment. The GD device employs a number of independent discharges, each one producing

atomic emission characteristic of the sample surface beneath it. Hadamard transform spatial imaging is used to multiplex the individual emissions onto a single detector and recover them from the multiplexed measurements.

The new system has several probable advantages over the traditional methods, including lower cost, smaller matrix effects, and smaller spectral and chemical interferences, as well as superior analytical precision and spatial resolution. Although to date the highest demonstrated spatial resolution is on the order of a millimeter (several times better than the traditional methods), we project that resolution on the order of a few microns may be attainable with the use of suitable source and optics. Therefore, resolution should be readily adjustable from macro- to micro-scales. This is important since these SRMs are being used outside NIST for applications which require sub-millimeter resolution, a market for which the SRMs may be unsuitable, since the homogeneity assessment is performed at super-millimeter resolutions. One could foresee the system being used to certify SRMs with homogeneity assessment geared to specific markets.

This year, initial experiments involving the compositional mapping of a steel-implanted brass surface were performed with an existing GD source modified for that purpose. The experiments demonstrated promise, but indicated the need for further source and optics development. Therefore, a prototype GD source and appropriate optics were designed and partially constructed. The construction and characterization of the new system continues, with particular effort devoted to the comparison of results with those of the traditional methods. As the spatial resolution of the system is extended to smaller dimensions, there will be a need for further source and optics development.

#### 4. The Development of Low-conductivity Reference Solutions from 5-20 $\mu\text{S}/\text{cm}$

Y.C. Wu

The generation of power through steam requires close monitoring of the purity of the boiler water. If water quality conditions are not met, the high generation rates and high temperatures lead to rapid corrosion and equipment failure. The U.S. Navy monitors and controls the quality of its shipboard feedwater and boiler water as part of its preventive maintenance program. Conductivity is used as an on-line measure of ionic contaminants in water. On-line sensors are calibrated both by on-board measurements and by less frequent land-based laboratory measurements. The purpose of this investigation was to develop simple, stable reference solutions of low conductivity, which could serve as standards for laboratory based calibration and quality assurance measurements. The theoretical value for the conductivity of pure water at 25 °C is 0.055  $\mu\text{S}/\text{cm}$ . Owing to the absorption of the ambient  $\text{CO}_2$ , the conductivity value for the  $\text{CO}_2$  contaminated water increases by a factor of 10 to 20, depending on the concentration of  $\text{CO}_2$  in the atmosphere. In our laboratory, the conductivity of pure water equilibrated with  $\text{CO}_2$  varies from 0.7 to 1.2  $\mu\text{S}/\text{cm}$ . Obviously, high quality water will have a very low conductivity which is in the neighborhood of 1  $\mu\text{S}/\text{cm}$ . If the water is contaminated with a minute amount of ionic



substance, for example 1 ppm of  $\text{CaCl}_2$ , the conductivity will be about  $3 \mu\text{S/cm}$ . More significant levels of contamination can easily register conductivities in the 20 to  $30\text{-}\mu\text{S/cm}$  range. Hence, low conductivity standards, in the range of 5 to  $30 \mu\text{S/cm}$ , are necessary.

The required accuracy for the application of these standards (for water quality control) is about  $\pm 1$  to 2% relative, which is well within the inherent precision of commercially available conductivity measuring equipment. In order to calibrate to the required accuracy, conductivity standards with accurately known specific conductivity, ( $\kappa$ ) must be available. Calibration of a reference conductivity cell can be accomplished using two such standards with accurately known  $\kappa$ 's, measuring the resistance of the cell (R), and determining the cell constant (G). Starting materials for low conductivity standards should be of known purity and stability.

A non-aqueous solvent was chosen to minimize the effect of dissolved  $\text{CO}_2$  on the conductivity. A 30% 1-propanol-water mixture combined with either KCl or benzoic acid as an electrolyte proved to be good candidate choices. The standard solutions can be easily prepared by weight, and these two chemicals are readily available as high purity materials. Two series of conductivity measurements were performed at  $25^\circ\text{C}$  and at a given time. About a month later, the measurements were repeated to test the stability of these solutions. Two solutions, one from each series, were measured at three temperatures: 20, 25 and  $30^\circ\text{C}$ , to evaluate the temperature coefficient of the conductivity at this temperature range. The results indicate that the conductivity range of interest can be covered by the appropriate concentrations of electrolyte in the solvent. Both sets of results are a linear function of molality. The temperature coefficients are about 2 to 3% per degree, therefore, they can be used under laboratory conditions without sacrificing much of the required accuracy. The solutions are fairly stable, exhibiting from 0.5% to 1% change over the one-month measurement period. A list of concentrations in molality and in weight percent for the round values of the standards is given in the following table:

$\kappa$ ( $\mu\text{S/cm}$ )	KCl		Benzoic Acid	
	Molality $\times 10^{-3}$	Weight %	Molality $\times 10^{-3}$	Weight %
5.0	0.0729	0.000543	0.176	0.00215
10.0	0.151	0.00113	0.704	0.00859
10.0	0.230	0.00171	1.58	0.0193
20.0	0.308	0.00230	2.81	0.0343
25.0	0.386	0.00288	4.40	0.0537

5. The Integration of Classical Chemistry and Instrumental Analysis for the Certification of a Sulfate Anion Standard Reference Material

T.W. Vetter, C.M. Beck II, and T.A. Butler

A classical method for the determination of sulfate that uses the precipitation of barium sulfate by has been coupled with the instrumental determination of trace sulfate and precipitate contaminants to decrease the analysis time in a sulfate anion solution standard (SRM 3181), while at the same time increasing accuracy and precision. Modifications were made to the classical technique to reduce loss of sulfate to the filtrate, contaminants in the precipitate, and volatilization of sulfate with the ignition of the precipitate.

Sulfate in a solution of potassium sulfate is separated by reverse precipitation with barium chloride in very dilute hydrochloric acid. Barium sulfate is filtered, ignited and weighed to determine sulfate gravimetrically. Instrumental methods were used to quantify any sulfate in the filtrate, contaminants in the precipitate, and volatilized sulfate. Any  $\text{BaCl}_2$  or  $\text{K}_2\text{SO}_4$  present in the barium sulfate precipitate was determined using coulometry for the chloride and flame atomic emission spectrometry (FAES) for the potassium. Loss of sulfate as  $\text{H}_2\text{SO}_4$  during the ignition of the precipitate is determined indirectly through the determination of  $\text{K}_2\text{SO}_4$ . Sulfate remaining in the filtrate is determined by inductively-coupled plasma mass spectrometry (ICP-MS).

The gravimetric determination by itself yields a mean result of  $1001.8 \text{ mg kg}^{-1} \text{ SO}_4$  with a standard deviation of the mean of  $0.32 \text{ mg kg}^{-1}$ . Average relative corrections of  $+0.01\%$  for mechanical loss,  $-0.29\%$  for  $\text{BaCl}_2$  in the precipitate,  $+0.03\%$  for  $\text{K}_2\text{SO}_4$  substituting for  $\text{BaSO}_4$  in the precipitate,  $+0.38\%$  for  $\text{SO}_4$  in the filtrate, and  $+0.06\%$  for volatilized sulfate, yield a mean result of  $1003.8 \text{ mg kg}^{-1} \text{ SO}_4$ . The actual corrections were measured and made on a sample-by-sample basis, resulting in a standard deviation of the mean of  $0.18 \text{ mg kg}^{-1}$ . The overall precision of the combined low-precision instrumental values and high-precision gravimetric values ( $\text{RSD} = 0.018\%$ ) is better than the precision of the gravimetric values ( $\text{RSD} = 0.032\%$ ) alone. This improved precision indicates that by correcting the biases detected in individual samples, the overall bias of the analysis can be significantly reduced. Despite the poorer precision and accuracy of the instrumental methods, the overall precision and accuracy of the sulfate determination is actually improved, since the instrumental methods are used to determine only a very small part of the analyte. After calculating for all sources of random and systematic uncertainty, the overall uncertainty of the method is below  $0.2\%$  relative.

6. The Development of Lead in Paint and Lead in Dust Standard Reference Materials

J.R. DeVoe, P.A. Pella, and A.F. Marlow

The Inorganic Analytical Research Division in cooperation with the Standard Reference Material Program and the Environmental Protection Agency (EPA) is currently developing a series of lead

in paint and lead in household dust Standard Reference Materials (SRM). These SRMs are intended for the calibration of instrumentation used for the direct solids analysis methods such as x-ray fluorescence (XRF) spectrometry, and as control materials for the development and evaluation of other methods of analysis. They are also intended for benchmarking the accuracy of secondary reference materials produced outside NIST. The three lead-based powdered paints being developed have target lead values of 0.05%, 0.5%, and 5.0%, respectively. The raw paint material was collected by EPA from painted interior surfaces of old buildings and shipped to NIST. The material was then processed in small batches, tested for lead content by x-ray fluorescence, categorized according to lead level, and then blended to produce an SRM having the appropriate nominal lead level. SRM 2582 (0.05% Pb) is already bottled and is now undergoing certification analysis by high accuracy isotope-dilution mass spectrometry. We also expect to complete SRM 2580 (5.0% Pb) in 1994.

In addition to paint, household dust collected by vacuum cleaners in both residential and hotel/motel buildings is being processed at NIST to serve as an SRM. This material will have a target lead value of about 100-200  $\mu\text{g/g}$ . The contents of each vacuum bag are first sampled and tested to determine lead levels. Bags containing similar lead levels are combined and the material is passed through a 100  $\mu\text{m}$  sieve to produce the final material suitable for blending. From pilot studies, it was decided that sieving the dust through a 100  $\mu\text{m}$  screen provides a good compromise between producing a sufficiently homogeneous material and an adequate yield of usable dust from each vacuum bag. In addition to lead, this SRM will be analyzed for other toxic elements such as mercury, cadmium, chromium, arsenic, and nickel.

## 7. Automated Flow-injection Analysis for the Determination of Arsenic and Selenium in Standard Reference Materials

**R. Saraswati (Ministry of Science and Technology, India) and R.L. Watters, Jr.**

Automated Flow Injection analysis (FIA) has been used to perform complex chemical preparation and analysis steps associated with hydride generation and atomic absorption spectrometry. In a typical flow injection manifold, a sample of about 100  $\mu\text{L}$  is introduced into the sample carrier stream which combines with streams of reagents and facilitates reactions and/or separations. When compared to manual wet chemical analytical procedures, FIA methods provide improved precision, decreased time per analysis, lower reagent consumption and better safety. Automated FIA has greatly increased the accuracy, precision, and throughput of hydride generation of arsenic and selenium determinations.

A flow-injection atomic absorption spectrometric method was developed for the determination of trace amounts of arsenic and selenium in a variety of proposed standard reference materials (SRMs). The samples were digested with  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$  using a reflux column. A thorough study of the effects of carrier solution, reducing agent, and carrier gas flow on the

matrix and absorbance of arsenic and selenium was conducted. The effect of the concentration of various acids on the hydride generation was also studied in detail.

Results were obtained for arsenic and selenium for six proposed SRMs covering a range of concentrations from 0.07  $\mu\text{g As/g}$  to 137.6  $\mu\text{g As/g}$ , and 0.05  $\mu\text{g Se/g}$  to 17.3  $\mu\text{g Se/g}$ . These results are summarized in the following table:

SRM	Name of SRM	Arsenic ( $\mu\text{g/g}$ )	Selenium( $\mu\text{g/g}$ )
1633b	Coal Fly Ash	137.6 $\pm$ 3.1	10.3 $\pm$ 0.4
1573a	Tomato Leaves	0.112 $\pm$ 0.003	0.054 $\pm$ 0.004
1570a	Spinach Leaves	0.074 $\pm$ 0.013	0.114 $\pm$ 0.007
1646a	Estuarine Sediment	6.405 $\pm$ 0.41	0.208 $\pm$ 0.028
2781	Domestic Sewage Sludge	7.88 $\pm$ 0.46	17.34 $\pm$ 1.07
1634c	Trace Elements in Fuel Oil	0.148 $\pm$ 0.007	0.104 $\pm$ 0.007

#### 8. The Systematics of Fully Resolved Spectral Linewidths in the Inductively Coupled Plasma Using Fourier Transform Spectroscopy

J.C. Travis, M.L. Salit, M.R. Winchester, and H. Porter (Brigham Young University)

The continued evolution of atomic emission spectroscopy towards increased accuracy and source optimization requires a detailed understanding of the physical processes at work in the plasma. The NIST UV/visible Fourier transform spectrometer (FTS) is capable of resolving spectral profiles in atmospheric plasmas with no discernable instrument function, and in low pressure plasmas with minimal instrument function. This capability, in conjunction with the broadband, multiplex nature of the instrument, is being used to study the systematics of spectral line shape in inductively-coupled plasma (ICP), direct current glow discharge (DCGD), and radio-frequency glow discharge (RFGD). Initial studies of model analytes with minimal hyperfine and/or isotopic structure are designed to highlight the systematic dependencies of the Doppler, collisional, and Stark contributions to the spectral width/shape on plasma conditions and atomic term designations.

To date the studies have raised more questions than provided answers. Doppler widths extracted from Voigt fits do not yield statistically consistent kinetic temperatures for all spectral lines present in either the ICP or the glow discharge. In the ICP, a smooth variation of predicted Doppler temperature with transition energy may imply shortcomings in the Voigt fit, possibly

resulting from asymmetric Lorentzian pressure and Stark broadening/shifts. This theory will be tested by improving the signal-to-noise ratio (SNR) of ICP spectra using ultrasonic nebulization and long integration times, and then examining the averages of replicate fit residuals for asymmetries and/or other significant deviations from the fit model. Once the energy-dependent bias in the apparent Doppler component is characterized, it should be possible to uncouple the Gaussian contribution from experimental profiles and reveal pressure and Stark effects directly.

For the glow discharge, both the Gaussian and Lorentzian components of the fit show a demonstrable dependence on the term designations of the transitions. For this low pressure plasma, which is not in local thermodynamic equilibrium (LTE) and has slow collision rates with respect to decay rates, line-specific "temperatures" may be indicative of kinetic processes involved in charge exchange, Penning ionization, or other effects. Under similar operating conditions (pressure and dissipated power), the Doppler behavior is the same for the DCGD and RFGD, but the Lorentz contribution is smaller in the RFGD, presumably reflecting a lower electron density and thus confirming Langmuir probe studies.

## 9. International Interlaboratory Comparison of the Chemical Analysis of Water

**J.R. Moody**

The International Measurement Evaluation Program is an IUPAC-sponsored effort to evaluate comparability and traceability of analytical chemical measurement. NIST has taken an active role in this program by supplying reference materials, both certified and candidate, as well as analytical measurements using the reference method of isotope dilution mass spectrometry. Eight trace elements in both a natural water and synthetic water were determined last year. The use of the SRMs in a program with over 60 participating (mostly European) laboratories has provided valuable exposure to the SRM program and potential for increased international usage of NIST SRMs.

The Standard Reference Material, Trace Elements in Water (SRM 1643c), is a popular SRM that is due to be recertified for the fifth time in 1994. It is a synthetic mixture in 2% nitric acid. One of the questions addressed by the interlaboratory experiment is the usefulness of this SRM as a calibrant for natural water. The conclusion reached from the evaluation of the interlaboratory results is that this synthetic standard cannot be used to normalize results for the natural water. In general, the inaccuracies in measurement were uncorrelated between the two materials. The results also illustrated the general lack of agreement among laboratories, often noted in chemical analysis. Since water is one of the simplest matrices that can be analyzed, these results illustrate the magnitude of the task of trying to achieve comparability of chemical measurement, in general, and international comparability, in particular.

The natural water reference material has been studied at NIST for stability and suitability for certification as a SRM. These inter-laboratory analyses gave NIST access to additional elemental

measurements that confirmed the long term stability of the material. At the 1993 IUPAC conference held in Belgium at which the program was discussed, considerable enthusiasm was generated by the program participants for the possibility of a natural water reference material. As a result, a natural water SRM will also be prepared and certified in 1994.

## 10. Fractionation Models and High Precision Measurements

J.D. Fassett and M.S. Rearick

High precision isotope ratio measurements have been developed at NIST to support an array of different programs. For instance, the technique of isotope dilution mass spectrometry (IDMS) is used for highly precise and accurate analysis of materials. In addition, NIST has maintained a long-term measurement program to evaluate the absolute isotopic abundances of elements, to better define the values for elemental atomic weights. Atomic weight experiments are characterized by a combination of highly precise chemical assay work and instrumental measurement. Separated isotopes are used to calibrate mass fractionation or isotopic discrimination during the measurement process. One of the tenets of isotopic ratio measurement is that isotopic fractionation is a process dependent on the relative difference in masses of the isotopes and that isotopic fractionation of one pair of isotopes can be used to predict the fractionation of other isotopes. Various mathematical models have been used, both linear and non-linear. However, when fractionation is relatively small, there is very little difference observed between the different models.

A discrepancy in the determination of the isotopic abundances of magnesium has existed for some time. The absolute isotopic abundances of magnesium were determined at NBS in 1966. Separated stable isotopes of  $^{26}\text{Mg}$  and  $^{24}\text{Mg}$  were used to calibrate the mass spectrometer. A triple filament procedure was used for ionization and the fractionation observed was about 0.5% per mass unit difference. In 1977, a group from California Institute of Technology (CIT) reported on a single filament, silica gel procedure for magnesium. This group used the NBS Mg isotopic standard and normalized the  $^{26}\text{Mg}/^{24}\text{Mg}$  ratio to the measured  $^{25}\text{Mg}/^{24}\text{Mg}$  ratio. The result for  $^{26}\text{Mg}/^{24}\text{Mg}$  equaled  $0.139805 \pm 0.000026$  which differs from the NBS value of  $0.13932 \pm 0.00026$  (both uncertainties are 2-sigma). The CIT measurement procedure was more precise, more sensitive, and exhibited higher fractionation (1.5% per mass unit difference). We have investigated high precision Mg isotopic measurement. Although the precisions achieved are not as tight as reported in these papers, we corroborated the basic results and reproduced the discrepancy in our laboratory. In addition, we have developed a procedure that exhibits the behavior within a single measurement. If the Mg is loaded onto two side filaments of a triple filament ionization source with silica gel, Mg is emitted at two disparate temperatures. At low temperatures, the CIT data is mimicked; at higher temperatures, fractionation is less and NBS values are measured. The technique is more sensitive and precise than the previously used NBS method. However, the failure to achieve consistent internal normalization is a puzzle and a problem. This new method also would seem to preclude an isobaric interference, another

potential explanation for the effect. The ramifications of these investigations are especially important in light of the planned atomic weight measurements of zinc using the single filament silica gel technique.

## 11. Determination of Magnesium in Estuarine Sediment and Spinach Leaves

**K.E. Murphy and P.J. Paulsen**

Certified elemental concentrations in Standard Reference Materials (SRMs) are required for accurate instrument calibration in the analysis of natural materials. In addition to quality control, SRMs provide an avenue of traceability for analytical laboratories. As part of the certification process, we recently determined the Mg concentration in two new SRMs: SRM 1646a, Estuarine Sediment and SRM 1570a, Spinach Leaves. The magnesium concentration was quantified by Isotope Dilution - Inductively Coupled Plasma Mass Spectrometry (ID-ICP-MS).

In this procedure an accurately known amount of the standard ( $^{26}\text{Mg}$ ) was mixed with samples of each material and the resulting  $^{24}\text{Mg}/^{26}\text{Mg}$  ratios were measured on the ICP-MS. The Mg concentration determined in the Estuarine Sediment was  $0.3882 \pm 0.0018$  % Mg/g (n=8, 1s) and the Mg concentration determined in the Spinach Leaf material was  $0.8706 \pm 0.0018$  % Mg/g (n=8, 1s). The concentration of the  $^{26}\text{Mg}$  standard solution was calibrated against gravimetrically prepared solutions of high purity Mg metal for each analysis. This provided the accuracy base of the method. The precision on the measurement of isotope ratios by the ICP-MS was on the order of 0.2%, which allowed for an assessment of the homogeneity of Mg in the material to this level. As indicated by the standard deviations listed above, the Estuarine Sediment had a higher degree of inhomogeneity than the Spinach Leaves.

In addition to providing the high level of accuracy and precision required for the certification of SRMs, the ICP-MS has the added advantage of high sample throughput. Mg was analyzed directly after dissolution and proper dilution without the need for chemical separations. The lack of molecular interferences in the Mg mass spectrum was proven by comparing the isotopic composition of pure Mg metal with the isotopic composition of Mg in the material. The coupling of isotope dilution with the ICP-MS greatly enhances the efficiency of isotope dilution as an analytical tool and opens the door for greater applicability of this inherently accurate technique.

## 12. Determination of Lead and Cadmium in Recycled Aluminum

**W.R. Kelly, R.D. Vocke Jr., and J.D. Fassett**

The recycling of aluminum cans makes good economic and environmental sense. However, recycling is not totally free of problems. About 60% of aluminum is recycled in the U.S. which means that after 6 cycles there is a high probability (>95%) that the aluminum article will be in a landfill. Aluminum cans rapidly dissolve in landfills releasing their trace elements into the

leachate which may find its way into the local groundwater. Virgin Al contains about 20 ppm of toxic elements such as Cd, Pb, Hg, and Cr<sup>+6</sup>, but these increase after each recycling step. Several northeastern states have adopted the model toxics in packaging legislation proposed by CONEG (Coalition of Northeastern Governors) which sets an upper limit of 100 ppm for these four elements in packaging materials. To meet the requirements of this legislation the aluminum industry requested Al standards certified for Pb and Cd at appropriate trace levels in alloys 3004 and 5182 which are used to fabricate the body and top of drink containers. The Aluminum Association, Inc. contracted with the Aluminum Corporation of America (Alcoa) to prepare these SRMs in the form of disks (diameter 63 mm, 19 mm thick) that would be suitable for calibration of optical emission and x-ray fluorescence techniques for the determination of Cd and Pb in recycled aluminum.

The Cd and Pb concentrations were determined in these alloys by isotope dilution thermal ionization mass spectrometry (ID-TIMS) here at NIST in cooperation with the American Society of Testing and Materials (ASTM). ID-TIMS is one of the most accurate and precise techniques for the determination of these elements. Pb and Cd were determined in chip samples from the same stock used to prepare the disks. Approximately 0.25 gram samples were spiked with <sup>206</sup>Pb and <sup>111</sup>Cd and then dissolved in high purity NIST HCl. Because of the large amount of Cd and Pb in these aluminum samples, only 10% of the sample was needed for the determination. Pb and Cd were chemically separated from the aluminum matrix in high yield and purity by anion exchange chromatography. The purified fractions were separated and loaded on Re filaments using silica gel as an ionization enhancer. The isotopic ratios were measured on a NIST designed 30-cm, 90-degree single sector, solid source mass spectrometer.

The mean Cd and Pb concentrations determined on six different samplings are given in the table below. The uncertainties are the standard deviation for a single determination. These ranged from 0.2% to 1.1% for Cd and 0.3% to 1.4% for Pb. The mass spectrometric measurement precision was about 0.1%; therefore, most of the uncertainty in the samples results from sample to sample variability.

SRM	Cd ppm (Mean ± 1s)	Pb ppm (Mean ± 1s)
<b>Alloy Type 3004</b>		
1710	8.435 ± 0.047	17.73 ± 0.23
1711	20.90 ± 0.12	63.89 ± 0.59
1712	51.65 ± 0.16	155.9 ± 2.1
<b>Alloy Type 5182</b>		
1713	8.778 ± 0.034	17.115 ± 0.052
1714	20.133 ± 0.039	65.33 ± 0.59
1715	50.19 ± 0.55	150.9 ± 2.6



### 13. Preparation and Calibration of Isotopic Spikes for the CIPM Metrology in Chemistry Round Robin

E.S. Beary, C.M. Beck II, J.D. Fassett, P.J. Paulsen, and R.L. Watters, Jr.

The International Bureau of Weights and Measures (BIPM) was chartered by the Convention of the Meter to ensure world-wide unification of physical measurements and standards. The U.S. is one of the original signatory nations to the Convention and participating member of the CIPM, the committee that supervises BIPM. In 1990 a Working Group of the CIPM was established to "advise the CIPM on whether or not the BIPM should have a significant role in addressing the problem of providing uniformity and traceability in chemical and physicochemical measurements." This action was taken in response to the concern that increased international uniformity and accuracy are required for the progress of advanced technology and the recognition that a significant proportion of industrial production and international trade is dependent on analytical chemical measurements.

The Working Group has proposed an exploratory program of cooperative work among leading national metrology laboratories and 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, coordinating the preparation and distribution of the unknown samples, and providing 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 unknown samples were prepared from primary reference materials, in a manner similar to a class of Solution Standard SRMs. The gravimetrically calculated concentrations were taken as target values and the stated goal of the exercise is to be within  $\pm 1\%$  of these target values. The results for the experiment have been submitted and are being evaluated at NIST. However, it is the policy of the CIPM not to divulge the results until the official report is prepared and presented. It is expected that this experiment will provide the framework for future work as well as for assessment of the present state-of-the-art for measurement comparability, at least by the technique of IDMS. Cooperative action by the national metrology laboratories will result in improvement of the state-of-the-art and lead to better comparability for increasingly demanding chemical measurements.

#### 14. Concentration and Profile Determination of Boron, Nitrogen, and Oxygen in Microelectronic Materials Using Cold Neutron Depth Profiling

R.G. Downing and G.P. Lamaze

Increasingly, manufacturers of semiconductor components are finding neutron depth profiling (NDP) to be an important tool for calibration, quality control, and basic research. This year a boron implant in silicon (SRM 2137) was issued for calibrating secondary ion mass spectrometers. Because NDP is both quantitative and nondestructive, NDP was used to certify the boron concentration in these standards. In addition, NDP simultaneously obtains a near surface depth profile of the boron distribution, albeit at slightly less resolution than SIMS. However, the use of NDP gives greater confidence in the SIMS profile of this SRM which is provided for information value as part of the certificate.

In recent independent collaborations with Sematech and Intel, NDP was used to standardize optical- or chemical-based analytical techniques for boron determinations. These published results compare the data from electrophoresis capillary chromatography, fourier transform infrared spectrometry (FTIR), and  $\mu$ -FTIR with those found using NDP. Similarly, we are engaged in a study with a commercial analytical lab comparing boron analysis from ion coupled plasma - Auger electron spectrometry and NDP. The goal of these efforts is to make in-house analytical techniques reliable enough for rapid quality control measurements on the product line of the manufacturer. The work is especially important in regulating boron in borophosphosilicate glass (BPSG) passivation layers, a very common component in semiconductor devices. Furthermore, manufacturers of instrumentation for depositing BPSG now use NDP to improve deposition uniformity within their chemical reactors.

Water can compromise the function of semiconductor circuitry and is known as a reliability hazard. Water can move laterally at cleave-planes and vertically through the capping dielectric. Oxygen profiling is now possible in special cases with NDP due to the increased neutron beam intensity of the Cold Neutron Research Facility (CNRF). As a result, we have begun studying the migration and trapping of  $^{17}\text{O}$  tagged water in dielectric films in collaboration with Intel and Applied Materials. Although the work is preliminary, O profiles obtained by NDP are being obtained and used to understand the physics and chemistry of the process.

Finally, in a collaboration between Texas A&M University and the Nuclear Methods Group, a graduate student has been working at NIST to establish time-of-flight NDP (ToF-NDP). This method of more precisely determining the residual charged particle energy of neutron induced reactions can consequently help create higher resolved depth profiles. Immediate applications are to be found in profiling nitrogen in SiN dielectric films a few hundred nanometers thick which are of great interest in designing semiconductor devices.

## 15. Effects of Target Temperature on Analytical Sensitivities of Cold Neutron Capture Prompt Gamma-Ray Activation Analysis

E.A. Mackey

Neutron scattering by H causes changes in the analytical sensitivities (cps/mg) of both thermal neutron (TN) and cold neutron (CN) capture prompt gamma-ray activation analysis (PGAA). These changes in sensitivity are measurable at concentrations of about one weight percent of H (and greater), so that for accuracy in the analysis of biological or other hydrogenous materials these effects must be characterized. For TN PGAA, these effects have been studied. The magnitude of the effect of scattering on element sensitivity is a function of the size, shape, and scattering power of the target. The effects of thermal neutron scattering on analytical sensitivities can be quantitatively accounted for by elastic scattering, i.e., scattering in which the average energy of the neutrons does not change. Effects of elastic scattering are minimal for a sphere. When there is no net change in the energy of the neutrons, spherical targets are preferred because sensitivities are constant as a function of size and hydrogen concentration.

Effects of neutron scattering on analytical sensitivities of CNPGAA are different from those of TNPGAA. Results of these initial studies indicate that cold neutrons interacting within a room temperature target, on average, gain energy upon scattering. An increase in the average energy of the neutrons corresponds to a decrease in absorption cross-sections and, therefore, decreased sensitivities. Experiments were designed to determine whether cooling the target would alleviate the part of the CNPGAA sensitivity decrease that is due to neutron warming; i.e., if the temperature of the target and the "effective temperature" of the neutron beam were similar, there would be little or no change in the average energy of the neutrons. CNPGAA sensitivities for H were measured for spherical and disk-shaped targets of tris-hydroxymethyl-aminomethane (9.15% H) at room temperature and after cooling, under vacuum, to liquid nitrogen temperature (77 K).

Cooling the targets resulted in increased sensitivity for all targets measured. Sensitivities for disks show the same qualitative trends for targets at 300 K and 77 K, but with a smaller sensitivity decrease for the 77 K targets. Sensitivities for H in the 300 K spheres decrease with sphere size but those at 77 K are constant within the uncertainties associated with counting statistics and target positioning in the beam. Constant sensitivity for spherical targets of varying diameters indicates that there is no measurable change in the average energy of the neutrons. Cooling these targets appears to eliminate the sensitivity decreases that are due to an increase in the average energy of the neutrons. Neutron scattering, even without energy change, will alter the mean free path of the neutron within the target, so that the entire effect for disks will not be eliminated by controlling sample temperature. However, that part of the sensitivity decrease that is due to neutron warming is, at the very least, mitigated, and the remainder of the effect that is due to inelastic scattering can be studied using Monte Carlo methods.

## 16. Trace Element Bioaccumulation in Marine Mammal Liver Tissues

R. Demilrap and E.A. Mackey

The National Biomonitoring Specimen Bank (NBSB) is a collaborative project of the Inorganic and Organic Analytical Research Divisions with several other U.S. government agencies. The National Oceanic and Atmospheric Administration supports two marine mammal tissue banks that are maintained as part of the NBSB. An integral part of these banking projects is instrumental neutron activation analysis of selected subsamples. Over the past year, we have added to our trace element data base concentrations for approximately 30 elements in the liver tissues of six pilot whales, nine beluga whales, four harbor porpoise, and three bowhead whales. The data base that is evolving is useful for determining baseline levels for a variety of marine mammal tissues, and for detecting any long-term trends in the environment reflected by trace element status.

To determine whether contaminant elements accumulate in liver tissues of marine mammals, the data were analyzed in two ways: a concentration factor (the ratio of the concentration in liver tissue to that in sea water) was calculated from the average concentration for each element for each species, and concentrations for each animal within a species were plotted as a function of standard length. Although it is preferable to determine the relationship between age and concentration, age estimates are not yet available for these animals and other investigators have shown that there is a linear relationship between length and age for pilot whales up to 10 to 15 years old.

Concentration factors for elements in pilot whale and beluga whale liver tissues fall into three general categories: electrolytes with the lowest values ( $10^{-1}$  -  $10^1$ ), essential trace elements ( $10^2$  to  $10^4$ ) and contaminant elements Cd, and Hg (and Ag for beluga whales) with the highest values ( $10^5$  to  $10^6$ ). These results are consistent with the hypothesis that the contaminant elements Cd and Hg accumulate in the liver tissues.

Positive linear correlations for element concentration versus length were observed for Ag, Se, and Hg in pilot whales. Similar trends were observed for Ag, Se, V, and Hg in beluga whales for 13 of the 14 tissues measured. No correlation with length was observed for Cd which is thought to accumulate to some extent in the liver, and to a greater extent in the kidney, of humans. Correlations were not as strong for the mature beluga whales as for the younger pilot whales, probably because many of the beluga tissues were taken from larger mature animals for which length may not be a good indication of age. However, when concentration versus length is plotted separately for males and females, correlations improve markedly. This could be the result of differences between males and females in growth rates (e.g., a 4-m long male is generally 7 to 8 years of age whereas a 4-m long female may be 10-16 years), or in metabolic processes (lactating females lose some fraction of stored contaminant elements). These results show that Hg, Ag, and Se accumulate over time in both pilot and beluga whale liver and that V accumulates in beluga liver.

## 17. Evaluation and Design of Neutron Focusing Lenses for Nuclear Analytical Techniques

H. Chen (Argonne National Laboratory), D.F.R. Mildner, and R.G. Downing

Focusing of cold neutron beams onto an area less than 1 mm<sup>2</sup> has been demonstrated at NIST using neutron lenses composed of hundreds of polycapillary fibers. Two prototype lenses were constructed at the Kurchatov Institute, Moscow, Russia, and were tested at NIST through a cooperative research and development agreement (CRADA) between X-Ray Optical Systems (XOS), Albany, New York, and the Nuclear Methods Group. XOS has Advanced Technology Program funding from NIST for the development of x-ray and neutron focusing lenses. Such lenses are being studied at NIST for use with the analytical beam techniques of prompt gamma activation analysis (PGAA) and neutron depth profiling (NDP) to achieve better detection limits and higher spatial resolution.

We began the project seeking to understand the transmission properties of the individual glass polycapillary fibers. Several lots of fibers were manufactured to provide a variety of compositions, surface topographies, and geometrical properties. Their neutron transmission characteristics are being studied using neutron wavelengths in the range from 0.2 to 1.0 nanometers and as a function of incoming beam divergence. Since focusing is achieved by directing the output of many individual fibers to a common focal point, the measurement of neutron transmission at various deflection angles has been important in lens design. These studies have lead to more than ten theoretical and experimental publications during the past three years.

Although the first lens clearly demonstrated the feasibility of neutron focusing, the most dramatic results were recently obtained using a second lens. It is 100 mm in length and is composed of 919 borosilicate glass polycapillary fibers. Each fiber has a 55% fractional open area and contains 547 channels with an inner diameter of 14 micrometers. The focal length of the lens is 57 mm from the exit. Unlike the first lens which is twice as long, this lens easily fits into the PGAA station at neutron guide 7 (NG7) at the NIST Cold Neutron Research Facility. The intensity distribution of the beam at the focus is nearly a triangular shaped curve having a FWHM width of 0.5 mm. When normalized to the incident beam intensity, a peak gain of 40 was reached at the center of the spot (average gain of a factor of 20). This lens yielded the highest neutron flux yet observed in the project. In the central beam area of 0.5 mm<sup>2</sup>, an estimated flux level of  $3.6 \times 10^9$  n (cm<sup>2</sup>-s) thermal equivalent was achieved.

A similar lens has been designed at NIST using lead silica fibers specifically for use with PGAA. It is currently under construction at XOS. The lens will be installed in the lower portion of NG7, where neutrons exiting from an area 50 x 50 mm will be concentrated down to a < 1 mm diameter spot. We expect a peak gain of 80 in flux, significantly improving performance compared to all previously tested lens designs. The availability of this lens will have immediate application for hydrogen determinations in materials where high spatial resolution is required.

## 18. Hydrogen Determination by Cold Neutron Prompt Gamma Activation Analysis

R.M. Lindstrom and R.L. Paul

There has long been a need for reliable hydrogen determination at low concentrations. Neutron-capture prompt gamma-ray activation analysis (PGAA) has been used to determine hydrogen in a variety of samples. The technique is specific for hydrogen, and entirely nondestructive. The NIST system, constructed as part of the Cold Neutron Research Facility (CNRF), uses a pure beam of long-wavelength neutrons to induce the  $^1\text{H}(n,\gamma)$  reaction, which gives a characteristic gamma ray at 2223.23 keV. With cold neutrons the background is low, so the detection limit in some materials is below 10  $\mu\text{g}$ . Improvements underway (better shielding, controlled sample atmosphere, and Compton suppression) will improve the detection limit to better than 1  $\mu\text{g}$ .

The PGAA system has been used for the analysis of hydrogen in a number of samples originating from NIST programs and from academic and industrial laboratories with whom NIST collaborates. Hydrogen was measured in a 1- $\mu\text{m}$  phosphosilicate glass film on a silicon wafer; the sample mass was about 1 mg. The net hydrogen content corresponded to  $6 \pm 9$  wt % of water in the film. We measured  $235 \pm 30$   $\mu\text{g H/g}$  in a 234-mg sample of SRM 354 Titanium; the certified concentration is  $215 \pm 6$ . In iron the detection limit is currently about 30  $\mu\text{g/g}$ . On a larger scale, hydrogen was measured at several times higher than the permitted maximum in a nearly intact titanium alloy compressor blade from a failed jet engine.

Numerous specimens of pure and substituted  $\text{C}_{60}$  fullerenes have been analyzed for hydrogen (and simultaneously for other elements such as C, S, K, and Rb). With substituted fullerenes, we were often able to measure other elements. For example, the H/S molar ratio in a 160-mg sample of  $\text{C}_{60}(\text{SO}_4\text{H})_8$  was  $1.0 \pm 0.1$ , as expected. We have determined both the major alkali and impurity hydrogen in superconducting  $\text{K}_3\text{C}_{60}$  and its  $\text{K}_6$  and  $\text{Rb}_n$  analogs. In one sample we found  $0.9 \pm 0.2$  moles H per mole Rb, suggesting that the sample may have been exposed to moisture after its synthesis.

Accuracy in the analysis of trace hydrogen is limited chiefly at present by background. For hydrogen as a major element, such as in partially deuterated polymers, the major inaccuracy is the effect of neutron scattering on reaction rates. PGAA remains a rich topic for future work.

## 19. International Human Nutrition Project of Minor and Trace Element Intakes in Different Countries: Results from a Preliminary Evaluation

G.V. Iyengar (Biomaterial International Sciences, Inc.), R.M. Parr, J.T. Tanner, W.R. Wolf, and R.R. Greenberg

A coordinated research program was initiated by the International Atomic Energy Agency (IAEA) in 1985 and has been supported in the U.S. by the Food and Drug Administration

(FDA), Department of Agriculture (USDA), and NIST. The purpose of this project is to obtain reliable data on the average daily intakes of nutritionally important minor and trace elements from diets consumed in a number of developed and developing countries, namely Australia, Brazil, Canada, China, Iran, Italy, Spain, Sudan, Sweden, Thailand, Turkey, and the U.S. The measurement phase of the program, which included the analysis of about 450 total diet samples, has been completed and the data evaluation process is currently in progress.

This project has brought together scientists from three major U.S. agencies to pool their knowledge and to solve a problem requiring multidisciplinary expertise: USDA - planning dietary studies; FDA - sampling strategy; and NIST - analytical expertise. All three agencies are providing expertise for a meaningful interpretation of data. NIST has provided leadership in the various aspects of quality assurance, sampling, sample preparation, analysis, and data evaluation. Typical total diets have been collected in 15 countries where they were freeze-dried and, subsequently, transferred to the IAEA laboratory at Seibersdorf. Here, they were homogenized, divided into smaller aliquots, and then distributed to a network of experienced analytical laboratories (called reference laboratories) for the determination of individual analytes. The analytes of interest included practically all the minor and trace elements considered to be essential or of interest as possible food contaminants, viz. Al, As, Ca, Cd, Cl, Cr, Cu, F, Fe, Hg, I, K, Mg, Mn, Mo, Na, Ni, P, Pb, Se, Sn, V, and Zn. A variety of analytical techniques has been used including neutron activation analysis (NAA). The NIST Nuclear Methods Group has been one such reference laboratory using NAA to determine Cr, Fe, Hg, Mo, Se, Zn in all the samples, and Cd in selected groups of samples.

Since the diets collected in this project are for specific target populations, a number of interesting conclusions are already evident from the data. For example, none of the countries participating in this program succeeded in achieving the U.S. recommended dietary allowances (RDAs) for the essential elements Ca and Zn, and many failed for Mg and Se. In all countries, the actual intakes exceed RDAs for Cl, K, Mn, Mo, and Na, and many also for Cr. The variability in intakes among countries is less than a factor of two between the high and low values for Cr, Cu, K, Mg, and Zn, and greater than a factor of 4 for I, Mn, and Se. For As, three countries appear to exceed the provisional tolerable intakes for toxicity. However, if the As is organically-bound as in fish, the toxic effect is minimal. Apparent high intakes of Hg in the Iranian and Turkish studies may indicate a cause for concern and an extensive national study may be warranted.

The results of this investigation are of special significance to the World Health Organization which is currently using these findings to establish a revised set of global RDAs. These worldwide RDAs will be published in 1994.

## 20. Evaluation of a Robotic Sample Changer for Certification of SRMs by INAA

D.A. Becker

Trace element certification of reference materials requires a high degree of accuracy and precision from an analytical laboratory. Counting of the irradiated samples is a crucial aspect of the analytical process for neutron activation analysis (NAA). NIST has been certifying Standard Reference Materials (SRMs) for over 25 years using neutron activation analysis. During that time a variety of automatic sample changers have been available for use with instrumental and/or radiochemical neutron activation analysis to increase productivity. In many cases, the results obtained using automatic sample changers have been less than perfect, often with malfunctions and breakdowns adding to the difficulties. The Nuclear Methods Group has obtained a computer-controlled robotic sample changer (RSC) which is capable of holding different sizes and types of sample containers, and which has provided reliable operation for the past year. This system has been used to provide certification data for two Standard Reference Materials, SRM 1570a, Spinach, and SRM 1646a, Estuarine Sediment.

The basic system construction can be described as follows. The first part is the sample changer itself, which moves both vertically (more than 50 cm) and horizontally (up to six meters) along a highly stable fixed transport frame. This attaches to a universal sample holder which is capable of firmly holding (with attachments) the multiple types of sample containers we specified. Finally, the entire system is operated by a personal computer controller system. This controller system is then connected to a pulse-height analyzer (PHA) through a communication cable.

The reproducibility and reliability of the changer system have been extensively evaluated using several methods. The system can now reliably provide a repeatable positioning uncertainty of  $\pm 0.51\%$  (1s; n=12) at 3 mm distance from the detector, and 0.25% (1s) for a 5 cm counting geometry. No decrease in counting accuracy and precision has been observed for the two sets of real SRM samples positioned in the RSC, although selected sample holders are required for optimum precision. Further, the use of this RSC system has significantly improved utilization of the detector and increased the sample throughput of this counting system.

## 21. Development of COM I Standard Communications Protocol

G.W. Kramer and F.R. Guenther (835)

In 1990, NIST joined with interested parties from the private sector and other Government agencies to form the Consortium on Automated Analytical Laboratory Systems (CAALS) to foster the development and use of automation in analytical chemistry. From the CAALS viewpoint, fully automated analytical systems can best be constructed by interconnecting instrument modules designed specifically for machine-controlled system use--instead of human-operated, stand-alone devices--with controllers to form integrated workcells.



CAALS is focusing its efforts on the interfaces between the modules and the controller, for it is at such interfaces that standardized component behaviors become essential to system integration. Successful module-to-controller integration involves electronic interfaces for data and control/status interchange as well as physical interfaces for samples and materials. Since other groups, such as the Analytical Instrument Association, are developing standards for data interchange, CAALS has concentrated on the control/status and physical interfaces. To bridge the chasm created by the use of multiple computing platforms, operating systems, and physical links between instruments and controllers, CAALS has developed its CAALS-I Communication Specification.

The CAALS-I Communication Specification for module-to-controller messaging specifies a communication protocol (rules about who gets to talk and when) and a message syntax (how the messages are formatted). It does not describe message semantics (the content of messages). CAALS-I was created as part of an overall scheme to develop a modular approach to analytical system building, where components can be inserted as needed in a simple plug-and-play fashion without the expense and difficulties experienced in creating today's custom systems. Although the CAALS working group searched, it was not able to find a single, existing communication specification that met its requirements for analytical laboratory systems. CAALS-I was created from existing standards and current practices expressly minimizing incorporation of new, untested concepts. Currently, CAALS-I supports a variety of links (IEEE-488, RS-232, and DDE) and can be adapted to other connection schemes such as TCP-IP. By providing a client-server approach with guaranteed connectivity and error-free message delivery that is applicable to small, embedded microcontroller applications as well as larger computers, CAALS-I provides a generic communication scheme which cuts across operating system and computing platform barriers. Over the past summer, CAALS conducted an external review of CAALS-I to detect problems with and increase awareness of this Communication Specification. The formal document describing the specification is currently being written and is slated for completion in December.

Writing a specification is one aspect of the problem, but getting industry to accept it is yet another. To make using CAALS-I easier, and hopefully more appealing, CAALS is implementing its specification on a variety of computing platforms with several different links to provide actual working examples. These implementations will be made available as addenda (with both documentation and actual code) to the formal specification. At this time, implementations are being developed for modules using three different types of embedded microcontrollers, for both PC-based modules and controllers using Windows and for a Windows NT-based controller. A first generation compliance testing tool for modules, being created to evaluate the robustness of module implementations, will also be available as an addendum to the CAALS-I specification. Finally, a guide to implementing CAALS-I with suggested application programming interfaces for several computing environments and examples of single-tasking, multi-tasking, threaded, etc. implementations is planned for next year.

**C. Outputs and Interactions  
(Inorganic Analytical Research Division)**

**1. Publications**

Adriaens, A., Kelly, W.R., and Adams, F., "Error Propagation in Isotope Dilution Mass Spectrometry Using Pulse Counting Detection," *Anal. Chem.* 65, 660-663 (1993).

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## 2. Talks

Beary, E.S., "Certification of Toxic Metals on Filters, SRM 267d, Using ICP-MS Isotope Dilution," FACSS, Philadelphia, PA, October 15, 1992.

Beary, E.S., "High Accuracy Determination of Selected Transition Metals by ICP-MS," 35th Rocky Mountain Conference, Denver, CO, July 3, 1993.

Becker, D.A., "Use of a Robotic Sample Changer in the Certification of Several Biological Reference Materials by Instrumental Neutron Activation Analysis," International Conference on Nuclear Methods in the Life Sciences, Prague, Czech Republic, September 15, 1993.

Becker, D.A., "Quality Assurance in Neutron Activation Analysis Intercomparisons: Effectiveness Versus Effort," American Nuclear Society, San Diego, CA, June 21, 1993.

Becker, D.A., "Errors and Interferences in the Determination of Chromium in Biological Materials by Instrumental Neutron Activation Analysis," American Nuclear Society, San Diego, CA, June 22, 1993.

Becker, D.A., "Determination of Platinum and Palladium in NIST Automobile Catalyst SRMs by Instrumental Neutron Activation Analysis," American Nuclear Society, San Diego, CA, June 23, 1993.

- Berezansky, P.A., "Preparation and Stability of NIST Conductivity Standards for Industry," 23th Northeast Regional Meeting of the American Chemical Society, Boston, MA, June 22, 1993.
- Butler, T.A., "Production and Certification of Spectrometric Standard Solutions," EAS, Somerset, NJ, November 17, 1992.
- Chen, H., "Neutron and X-Ray Focusing Using Capillary Optics," 3rd European Conference on Accelerators in Applied Research and Technology, Orleans, France, September 3, 1993.
- Downing, R.G., "Neutron Depth Profiling Applications in Semiconductors," Small Accelerator Conference, University of Texas, Denton, TX, November 3, 1992.
- Downing, R.G., "Activities of the National Institute of Standards and Technology," Universidad de Concepcion, Departamento de Analisis Instrumental, Concepcion, Chile, November 20, 1992.
- Downing, R.G., "Neutron Analytical Techniques and Their Applications at NIST," Universidad de Chile, Departamento de Fisica, Santigao, Chile, November 27, 1992.
- Downing, R.G., "Particle and X-ray Detection Using the Video Radiation Detector," CID Technology, Liverpool, NY, March 31, 1993.
- Downing, R.G., "Advances in the Methods for Characterization of BPSG Films," 183rd Meeting of the Electrochemical Society, Honolulu, HI, May 16, 1993.
- Downing, R.G., "The Spatial Resolution of Water Diffusion and Trapping in Silicate-Glass Thin Films by Micro-FTIR and Neutron Depth Profiling," 183rd Meeting of the Electrochemical Society, Honolulu, HI, May 16, 1993.
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- Downing, R.G., "The Spacial Resolution of Water Diffusion and Trapping in Silicate Glass Thin Films by Micro-FTIR and Neutron Depth Profile," 183rd Mtg. of the Electrochemical Society, Honolulu, HI, May 19, 1993.
- Downing, R.G., "Sample Collection of Water and Biological Samples at Remote Location for Trace and Ultratrace Neutron Activation Analysis," Seminario Regional Sobre Aplicaciones de Los Isotopos Y Radiaciones para Paises de America Latina Y El Carbide, Commission Chilena de Energia Nuclear, Santiago, Chile, August 12, 1993.

- Downing, R.G., "Industrial Applications of Nuclear Technology," Seminario Para Ejecutivos - Aplicaciones de Techicas Nucleares Y Radiacion En La Industria, Comision Chilea de Energia Nuclear, Santiago, Chile, August 16, 1993.
- Downing, R.G., "Overview of the Analytical Neutron Beam Techniques at NIST," University of Santiago, Santiago, Chile, August 24, 1993.
- Downing, R.G., "NIST Neutron Depth Profiling and New NIST Depth Profiling Standard," Secondary Ion Mass Spectrometry (SIMS) Workshop, Sematech, Austin, TX , September 14, 1993.
- Fassett, J.D., "Traceability to the Mole: A New Initiative by CIPM," Euroanalysis VIII, Edinburgh, Scotland, September 8, 1993.
- Greenberg, R.R., "Application of Neutron Activation Analysis for the Certification of National Institute of Standards and Technology Biological Standard Reference Materials," Workshop on Standard Reference Materials, Hamdard University, New Delhi, India, February 6, 1993.
- Greenberg, R.R., "Use of Nuclear Analytical Techniques for Environmental and Food-Related Materials," 4th Intl. Conf. on Health and Disease: Effects of Essential and Toxic Trace Elements, Hamdard University, New Delhi, India, February 10, 1993.
- Greenberg, R.R., "Chemistry Problems for the Analysis of Chromium by Radiochemical Neutron Activation Analysis," American Nuclear Society, San Diego, CA, June 21, 1993.
- Greenberg, R.R., "Determination of Essential Elements in Dietary Reference Materials," 15th International Congress of Nutrition, Adelaide, Australia, September 27, 1993.
- Kelly, W.R., "Enriched Stable Isotopes of Sm as Intentional Tracers of Diesel and Residential Oil Furnace Emissions in Roanoke, VA," International Symposium on Measurement of Toxic and Related Air Pollutants, Durham, NC, April 8, 1993.
- Kelly, W.R., "Accurate and Precise Determination of Sulfur in Coal SRMs by TIMS," International Conference on Coal Utilization and the Environment, Orlando, FL, May 15, 1993.
- Kelly, W.R., "Tracing Emissions from Coal-Fired Power Plants with Enriched Rare Earth Isotopes," International Conference on Coal Utilization and the Environment, Orlando, FL, May 17, 1993.

- Kramer, G.W., "The Consortium on Automated Analytical Laboratory Systems," Society of Quality Assurance Annual Meeting, Atlanta, GA, October 1, 1992. Invited
- Kramer, G.W., "Creating Standards for Multivendor Laboratory Systems Integration," Scientific Computing and Automation Meeting, Crystal, City, VA, October 15, 1992.
- Kramer, G.W., "The Consortium on Automated Analytical Laboratory Systems," International Symposium on Laboratory Robotics and Automation, Boston, MA, October 27, 1992. Invited
- Kramer, G.W., "CAALS and its Modularity Project," Hewlett-Packard Co., Inc., Wilmington, DE, November 13, 1992.
- Kramer, G.W., "Overview and Focus on the Consortium on Automated Analytical Laboratory Systems (CAALS)," Joint Southeast and Mid-Atlantic Regional ACS Meeting, Crystal City, VA, December 9, 1992.
- Kramer, G.W., "The Consortium on Automated Analytical Laboratory Systems," American Chemical Society Analytical Topical Group, Wilmington, DE, December 12, 1992. Invited.
- Kramer, G.W., "Modular Instruments—The Path to Fully Automated Analysis Systems," Joint Meeting of the New York Society for Applied Spectroscopy and the North Jersey Chromatography Group, East Hanover, NJ, January 20, 1993. Invited
- Kramer, G.W., "CAALS and its Modularity Project," Boehringer Mannheim, Inc., Indianapolis, IN, February 4, 1993.
- Kramer, G.W., "CAALS and its Modularity Project," Rhône-Poulenc, Vitry-sur-Seine (Paris), France, February 15, 1993.
- Kramer, G.W., "CAALS-I Communication Specification," Poster Session, 2nd International Symposium on Laboratory Robotics and Artificial Intelligence Applied to Analytical Chemistry and Laboratory Medicine, Montreux, Switzerland, February 23-26, 1993.
- Kramer, G.W., "The NIST Consortium on Automated Analytical Laboratory Systems—Standards for Automated Systems Used in Analytical Chemistry," The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlanta, GA, March 9, 1993.
- Kramer, G.W., "Organic Synthesis Automation," Rhône Rorer, Collegeville, PA, April 21, 1993. Invited

- Kramer, G.W., "Modular Instruments—Building Blocks for Fully Automated Analysis Systems," Delaware Valley Automation Group, College, PA, April 21, 1993. Invited
- Kramer, G.W., "CAALS and its Modularity Project," Digital Equipment Corporation, Marlboro, MA, May 27, 1993.
- Kramer, G.W., "CAALS and its Modularity Project," Wellcome Foundation in Beckenham, England, June 15, 1993.
- Kramer, G.W., "CAALS and its Modularity Project," Process Analysis and Automation, Ltd., Farnsbrough, England, June 16, 1993.
- Kramer, G.W., "CAALS and its Modularity Project," ICI Wilton, Middlesbrough, England, June 17, 1993.
- Kramer, G.W., "CAALS Activities Update," DoE CAA Team Meeting, Lake Tahoe, CA, August 5, 1993.
- Kramer, G.W., "The NIST Consortium on Automated Analytical Laboratory Systems—Standards for Automated Systems Used in Analytical Chemistry," American Chemical Society Symposium on Emerging Technologies in Hazardous Waste Management, Atlanta, GA, September 27, 1993. Invited
- Lamaze, G.P., "Analysis of Cubic Boron Nitride Thin Films by Neutron Depth Profiling, European Conference on Diamond-like and Related Materials," Albufeira, Portugal, September 22, 1993.
- Lankosz, M., "Investigation of Geometrical Effects in X-ray Fluorescence Microanalysis of Geological Samples," 42nd Annual Denver X-ray Conference, Denver, CO, August 4, 1993. Invited
- Lindstrom, R.M., "The  $k_0$  Approach in Prompt-Gamma Activation Analysis,"  $k_0$  Users Workshop, Astene, Belgium, October 2, 1992.
- Lindstrom, R.M., "Guided Neutron Beams and Analytical Chemistry," North Carolina State University, Raleigh, NC, March 18, 1993.
- Lindstrom, R.M., "Accuracy in Gamma Spectrometry: Pulse Pileup, Dead Time, and Fast Electronics," American Nuclear Society Annual Meeting, San Diego, CA, June 22, 1993.
- Lindstrom, R.M., "Cold Neutron Beams and Chemical Analysis at NIST," Hungarian Academy of Sciences, Budapest Neutron Centre, Budapest, Hungary, September 8, 1993.

- Lindstrom, R.M., "Cold Neutron Beams and Chemical Analysis at NIST," Jozef Stefan Institute, Ljubljana, Slovenia, September 10, 1993.
- Lindstrom, R.M., "Analytical Applications of Guided Neutron Beams in the Life Sciences," International Conference on Nuclear Analytical Methods in the Life Sciences, University of Agriculture, Prague, Czech Republic, September 13, 1993.
- Lindstrom, R.M., "SUM and MEAN: Standard Programs for Activation Analysis," International Conference on Nuclear Analytical Methods in the Life Sciences, University of Agriculture, Prague, Czech Republic, September 15, 1993.
- Lindstrom, R.M., "Analytical Applications of Cold Neutron Capture and Opportunities for Nuclear Physics," 8th International Symposium on Capture Gamma-Ray Spectroscopy and Related Topics, University of Fribourg, Fribourg, Switzerland, September 22, 1993.
- Lindstrom, R.M., "Cold Neutron Beams and Chemical Analysis at NIST," Paul Scherrer Institute, Villigen, Switzerland, September 23, 1993.
- Mackey, E.A., "Determination of Tin in Human Liver Using Radiochemical Neutron Activation Analysis," 3rd International Conference on Nuclear and Radiochemistry, Vienna, Austria, September 9, 1992.
- Mackey, E.A., "Trace Element Concentrations in Marine Mammal Liver Tissues Archived at the National Biomonitoring Specimen Bank," 8th International Conference on Trace Elements in Man and Animal, Dresden, Germany, May 18, 1993.
- Mackey, E.A., "Trace Element Concentrations in Marine Mammal Liver Tissues Archived at the National Biomonitoring Specimen Bank," 8th International Conference on Trace Elements in Man and Animal, Dresden, Germany, May 19, 1993.
- Mackey, E.A., "Effects of Target Temperature on Analytical Sensitivities of Cold Neutron Prompt Gamma-Ray Activation Analysis," International Conference on Nuclear Analytical Methods in the Life Sciences, Prague, Czech Republic, September 14, 1993.
- Mildner, D.F.R., "Focusing Neutrons Using Capillary Optics," Physics Department, National Laboratory for Engineering and Industrial Technology, Sacavem, Portugal, October 22, 1992.
- Mildner, D.F.R., "Focusing Neutrons Using Capillary Optics," School of Physics and Space Research, Applied Physics Section, University of Birmingham, England, October 29, 1992.

- Mildner, D.F.R., "Low Resolution Small-Angle Scattering Using Neutron Focusing Optics," IX Intl. Mtg. on Small-Angle Scattering, Cilas-Alcatel Neutron Laboratory, Saclay, France, April 27, 1993.
- Murphy, K.E., "The Application of Isotope Dilution Mass Spectrometry to the Analysis of Lead in Standard Reference Materials," Indiana University of Pennsylvania Chemistry Department Seminar, Indiana, PA, March 5, 1993.
- Murphy, K.E., "Determination of Magnesium in Estuarine Sediment by Isotope Dilution - Inductively Coupled Plasma Mass Spectrometry," 35th Rocky Mountain Conference, Denver, CO, July 14, 1993.
- Paul, R.L., "Chemical Analysis of Fullerenes and Fullerene Compounds by Cold Neutron Prompt Gamma Activation Analysis," Spring Meeting of the Materials Research Society, San Francisco, CA, April 14, 1993.
- Paul, R.L., "Determination of Hydrogen in Titanium Alloy Jet Engine Compressor Blades by Cold Neutron Capture Prompt Gamma-Ray Activation Analysis," 12th Annual Review of Progress in Quantitative Nondestructive Evaluation, Bowdoin College, Brunswick, ME, August 2, 1993.
- Paul, R.L., "Measurement of Hydrogen by Cold Neutron Capture Prompt Gamma-Ray Activation Analysis," 206th American Chemical Society National Mtg., Chicago, IL, August 22, 1993.
- Paulsen, P.J., "Certification of Toxic Metals on Filters, SRM 267d, Using ICP-MS Isotope Dilution," 3rd International Conference on Plasma Source M.S., Durham, U.K., October 2, 1992.
- Paulsen, P.J., "Determination of Pt, Pd, Rh and Pb in Used Auto Catalysts - Analytical Procedures," 2nd National Conference on ICP-MS, Detroit, MI, September 8, 1993.
- Pella, P.A., "NIST Workshop on The Accuracy of Lead Measurements of Paint, Soil, and Dust Samples by Laboratory-Based X-Ray Fluorescence," University of Colorado, Boulder, CO, July 30, 1993.
- Pella, P.A., "Development of NIST Standard Reference Materials for Lead in Blood, Paint, Household Dust, Soil, and Simulated Bone," ASTM Boulder Conference, University of Colorado, Boulder, CO, July 28, 1993.
- Pella, P.A., "Geometrical and Matrix Effects in the X-Ray Microfluorescence Analysis of Individual Particles," 42nd Annual Denver Conference, Sheraton Denver Technology Center Hotel, Denver, CO, August 5, 1993.



- Pella, P.A., "X-ray Analysis of Lead in Paint, Soil, and Dust Using Compton Scatter for Matrix Correction," Australian X-ray Analytical Association, 9th National Schools and Conference, University of Queensland, Brisbane, Australia, September 27, 1993. Invited
- Pella, P.A., "Results of Analysis of Selected Reference Materials: A Comparison of XRF With Other Analytical Methods," Australian X-ray Analytical Association, 9th National Schools and Conference, University of Queensland, Brisbane, Australia, September 28, 1993. Invited
- Pella, P.A., "Plenary Lecture: Geometric and Matrix Effects in the X-ray Microfluorescence Analysis of Individual Particles," Australian X-ray Analytical Association, 9th National Schools and Conference, University of Queensland, Brisbane, Australia, September 29, 1993. Invited
- Pratt, K.W., "Automated High-Precision Coulometry at NIST," NASA Kennedy Space Center, Kennedy Space Center, FL, January 28, 1993. Invited
- Pratt, K.W., "Automated High-Precision Coulometry," 27th Middle Atlantic Regional Meeting, Hempstead, NY, June 2, 1993.
- Pratt, K.W., "Automated High-Precision Coulometry," 44th International Society of Electrochemistry Conference, Berlin, Germany, September 8, 1993.
- Salit, M.L., "Grafting Modularity onto Existing Instruments," The Scientific Computing and Automation Conference, Washington, DC, October 15, 1992.
- Salit, M.L., "The Inorganic Standard Reference Material Program at NIST," special presentation to Elf-Aquitane, The Cosmos Club, Washington, DC, December 9, 1992.
- Salit, M.L., "CAALS Modularity: Progress Towards Plug-N-Play Instruments," The Joint Southeast and Mid-Atlantic Meeting of the American Chemical Society, Crystal City, VA, December 11, 1992.
- Salit, M.L., "Applying ICP-OES to Analytical Problems Requiring a Total Uncertainty of 5 Parts Per Thousand," 1993 European Winter Plasma Conference, Granada, Spain, January 12, 1993. Invited
- Salit, M.L., "NIST CAALS: Controlling Automated Chemistry Workcells," The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlanta, GA, March 7, 1993.

- Travis, J.C., "Collective Determination of Kinetic Temperatures in Plasmas Using UV-Visible Fourier Transform Spectroscopy," XXVIII Colloquium Spectroscopicum Internationale, York, England, July 2, 1993.
- Travis, J.C., "Detection of Laser Produced Ions in Atmospheric Plasmas," Symposium for 1993 ACS Award in Spectrochemical Analysis (for Richard A. Keller), American Chemical Society, Chicago, IL, August 23, 1993. Invited
- Turk, G.C., "Laser-enhanced Ionization Spectroscopy in Flames and Plasmas," Institute of spectroscopy, Troitzk, Russia, October 5, 1992.
- Vocke Jr., R.D., "Standards in QA/AC," LEADTECH, Blood Lead Screening/Analysis Quality Symposium, Bethesda, MD, October 1, 1992.
- Vocke Jr., R.D., "Isotopic Reference Materials of ICP-MS and TIMS Analysis: Present Status and Future Prospects," PTB Colloquium, Braunschweig, Germany, December 10, 1992.
- Vocke Jr., R.D., "Rocks, Minerals and Age Dating," Adventures in Science, NIST, Gaithersburg, MD, May 6, 1993.
- Vocke Jr., R.D., "The Ice Man Cometh," Sigma Xi, Frederick, MD, May 21, 1993. Invited
- Vocke Jr., R.D., "Activities at NIST Pertaining to Atomic Weight and High Precision Isotopic Abundance Research," CAIWA, IUPAC General Meeting, Lisbon, Portugal, August 7, 1993.
- Watters Jr., R.L., "Comparability and Traceability of Chemical Measurements Related to Lead in the Environment," ASTM Boulder Conference, University of Colorado, Boulder, CO, July 29, 1993.
- Winchester, M.R., "Glow Discharge Atomic Emission Imaging of Solid Surfaces," New Developments in Glow Discharge Spectroscopy Symposium, Atlanta, GA, March 9, 1993.
- Winchester, M.R., "Fourier Transform Atomic Emission Spectroscopy—Problems, Solutions and Applications," Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN, August 13, 1993.

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

Advancement of the Quality of Clinical Laboratory Work in the United States, W.F. Koch  
Collage of American Pathologists (CRADA)

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)

Capillary Optics to Control Neutrons for Boron Neutron Capture Therapy, R.G. Downing  
X-Ray Optical Systems, Inc. (CRADA)

Consortium on Automated Analytical Laboratory Systems, G.W. Kramer  
ABC Laboratories, Inc. (CRADA)  
Boehringer Mannheim, Inc. (CRADA)  
BP America (CRADA)  
CEM Corporation (CRADA)  
Department of Energy and the National Laboratories  
Digital Equipment Corporation (CRADA)  
E.I. duPont de Nemours Company, Inc. (CRADA)  
Eastman Kodak Company (CRADA)  
Environmental Protection Agency  
Hewlett-Packard Company (CRADA)  
Occidental Chemical Corporation (CRADA)  
The Perkin-Elmer Corporation (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)

Possibility of Enhanced Utilization of Pencil-Type Discharge Lamps, M.L. Salit  
Oriental Corporation (CRADA)

#### 4. Patent Awards and Applications

Kingston, H.M., Riviello, J.M., and Siriraks, A., "System for Detecting Transition and Rare Earth Elements in a Matrix," Patent No. 5,244,634 (Issued September 1993).

#### 5. SRM Activities

113b	zinc-ore concentrate	1731	Ti alloy
191a	sodium bicarbonate pH	1732	Ti alloy
192a	sodium carbonate pH	1733	Ti alloy
648	TI (5AL-2SN-2ZR-4C4-4MO)	1819a	sulfur in lubricating base oil
918a	sodium chloride-clinical	1930	glass filters, extended
924a	lithium carbonate	1941a	organics in marine sediment
930	glass filters-visible	2030	glass filters
930a	glass filters-visible	2031	metal-on-quartz filters
930b	glass filters-visible	2034	holmium oxide
930c	glass filters-visible	2135m	Ni-Cr depth profile standards
930d	glass filters-visible pH	2175	Ni-Cr-Mo high temperature alloy
931e	liquid filters-UV-visible	2556	pellet auto catalyst
999a	potassium chloride	2557	monolith auto catalyst
1084a	wear metals in oil, 100 P	2580	lead in paint
1085a	wear metals in oil, 300 P	2581	lead in paint
1165	petroleum coke	2582	lead in paint
1166	foundry coke	2692a	sulfur in coal
1167	malleable coke	2709	San joaquin soil
1570a	spinach leaves	2710	Montana I soil
1573a	tomato leaves	2711	Montana II soil
1633b	coal fly ash	2775	malleable coke
1634c	trace elements in fuel oil	2776	foundry coke
1641c	mercury in water-concentration	2781	domestic sewage sludge
1646	estuarine sediment	2782	coke
1646a	estuarine sediment	3004	spectrometric solution
1710	aluminum alloy	3101a	spectrometric solution
1711	aluminum alloy	3102a	spectrometric solution
1712	aluminum alloy	3103a	spectrometric solution
1713	aluminum alloy	3107	spectrometric solution
1714	aluminum alloy	3108	spectrometric solution
1715	aluminum alloy	3109a	spectrometric solution

3110	spectrometric solution	3150	spectrometric solution
3111a	spectrometric solution	3151	spectrometric solution
3112a	spectrometric solution	3152a	spectrometric solution
3114	spectrometric solution	3153a	spectrometric solution
3117a	spectrometric solution	3154	spectrometric solution
3118a	spectrometric solution	3156	spectrometric solution
3120	spectrometric solution	3158	spectrometric solution
3124a	spectrometric solution	3161	spectrometric solution
3127a	spectrometric solution	3162a	spectrometric solution
3128	spectrometric solution	3165	spectrometric solution
3129a	spectrometric solution	3167a	ectrometric solution
3131a	spectrometric solution	3172a	multielement mix b solution
3132	spectrometric solution	3179	multielement mix
3133	spectrometric solution	3181	sulfate anion solution
3134	spectrometric solution	3183	anion solution, fluoride
3136	spectrometric solution	3190	electro conductivity 25
3140	spectrometric solution	3191	electro conductivity 100
3141a	spectrometric solution	3192	electro conductivity 500
3142a	spectrometric solution	3193	electro conductivity 1000
3144	spectrometric solution	3195	electro conductivity 100,000
3148a	spectrometric solution	3196	electro conductivity 200,000

Analytical services have been provided for the following:

Carnegie Institute of Washington  
 Enfield Industrial  
 J.T. Baker, Inc.  
 John Hopkins University  
 KPMG Peat Marwick  
 Lawrence Livermore National Laboratory  
 McClellan Air Force Base  
 Sussex University (United Kingdom)  
 University of Maryland  
 U.S. Geological Survey

## 6. SRD Activities

Ames Atlas

## 7. Calibrations

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

3M Company (SD)	GTE North
3M Company (MN)	GTE Products Corporation
Abbott Laboratories (IL)	Hach Company
Abbott Laboratories (TX)	Henkel Corporation
Abbott Puerto Rico Operations	Hitachi Instruments, Inc.
Allied Signal, Inc.	Hyperion, Inc.
Amgen, Inc.	ICI Pharmaceutical Group
Augusta Service Co.	IMCO Group
Bacharach, Inc.	Institut Berlin (Germany)
Barre-National, Inc.	Isolab, Inc.
Bausch & Lomb	JBL Scientific, Inc.
Baxter Healthcare Corporation	John Dempsey Hospital
Beckman Instruments	Johnson & Johnson Medical
Bio Systems Laboratory	Juliette Metrology Laboratory
Bioanalytical Instruments	Kabi Vitrum, Inc.
Boehringer Mannheim Corporation	Litton Bionetics
CIBA-GEIGY Corporation (NJ)	Massachusetts Institute of Technology
CIBA-GEIGY Corporation (NY)	Marion Co.
Cal Check	Merck & Co., Inc.
Cephalon, Inc.	Miles Diagnostic Corporation
Chelsea Laboratories, Inc.	Miles, Inc.
Corion Corporation	Milliken Chemical Blacksburg Plant
Coulter Corporation	Milliken Chemical Dewey Plant
Cygnus Research Corporation	Milliken Chemical Spartanburg Plant
Del Scientific, Inc.	National Standards
Dynatec Labs, Chantilly, VA	Naval Air Warfare Center
E.I. duPont de Nemours & Co. (NC)	OCA
E.I. duPont de Nemours & Co. (NY)	Organon Teknika
E.I. duPont de Nemours & Co. (VA)	Oxford Labware
Electric Power Research Institute	Parke-Davis
Eastman Kodak Company (CO)	Perkin-Elmer Corporation (CT)
Eastman Kodak Company (NY)	Perkin-Elmer Corporation (MI)
Eli Lilly & Company	Perkin-Elmer Corporation (NJ)
Enfield Industrial Corporation	Perkin-Elmer (The Netherlands)
Ethicon, Inc.	Pet, Inc.
Finnish Red Cross (Helsinki)	Pfizer, Inc. (NY)
Food & Drug Administration (NY)	Physicians Medical Laboratory
Food & Drug Administration (OH)	Repligen Corporation
Foran Spice	Rex Hospitals, Inc.

Roche Products, Inc.  
Sanofi Winthrop  
Schwan's Sales  
Shimadzu Scientific Instrument  
Shipley Co., Inc.  
Sigma Chemical  
Smith Kline Beecham  
Stabro Laboratories  
Sterling Winthrop  
Sun Chemical Corporation  
Syva Company  
Tennessee Eastman Kodak  
The Concentrate Manufacturing  
U.S. Army Research Laboratory  
UOP, Inc.  
USCI Division  
USPC  
Union Carbide C&P Co., Inc.  
Varian Associates  
Whitehall Robins  
Witco Corporation

## **8. Committee Assignments**

### **E.S. Beary**

EEO Representative, CSTL  
SNM Custodian, CSTL

### **C.M. Beck II**

ASTM, E01 Chemical Analysis of Metals, Ores, and Related Materials  
ASTM, SC.02 Ores, Concentrates and Related Metallurgical 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, E-10 Nuclear Technology and Applications  
ASTM, SC.05 Nuclear Radiation Metrology  
ASTM, WG.08 Nuclear Environmental Metrology  
ASTM, E10 Nuclear Technology and Applications

ASTM, SC.05 Nuclear Radiation Metrology  
ASTM, WG.10 Neutron Metrology  
ASTM, WG.12 Nuclear Methods of Chemical Analysis, Chairman

**P.A. Berezansky**  
IARD Lunch Bunch Committee

**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, E10 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  
CSTL Colloquia Committee

**M.S. Epstein**  
National Capital Area Skeptics, Board of Directors (Vice President)  
EPA Working Committee on Lead-Based Paint Good Lab Practices Guide  
Society for Scientific Exploration Annual Meeting, Program Committee  
Subcommittee on Control of Proanalytical Variation in Trace Metal Analysis, National Committee for Clinical Laboratory Standards  
Society for Scientific Exploration, Governing Council  
Montgomery Area Science Fair (1993) (Judge)  
Interagency Working Group on Environmental Technologies  
FCCSET Subcommittee on Environmental Technologies  
CSTL Electronic Notebook Policy Committee (Chairman)

**R.F. Fleming**  
ASTM, E10 Nuclear Technology and Applications  
ASTM, SC.05 Nuclear Radiation Metrology  
ASTM, SC.07 Radiation Effects on Materials  
ASTM, WG.04 Radiation Metrology for Food Processing  
National Steering Committee for the Advanced Neutron Source

**R.R. Greenberg**  
ASTM, E10 Nuclear Technology and Applications  
ASTM, SC.05 Nuclear Radiation Metrology



ANS, Trace Analysis Committee, Division of Biology and Medicine  
ANS, Executive Board, Division of Biology and Medicine  
NIST Radiation Safety Committee

**W.R. Kelly**

NIST Colloquium Committee  
NIST Sigma Xi Program (Chairman)

**W.F. Koch**

Analyst CSTL, NIST Program Office  
NCCLS, C004 Board of Directors  
NCCLS, CO16 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.W. Kramer**

ASTM, E31 Computerized Systems  
ASTM, SC.40 Laboratory Information Management Systems  
ASTM, E49 Computerization of Material Property Data  
ASTM, SC.52 Experimental Data Interchange  
NIST Electronics Storeroom Committee

**G.P. Lamaze**

ASTM, EO10 Nuclear Technology and Applications  
ASTM, SC10.95 Long Range Planning  
ASTM, SC.05 Nuclear Radiation Metrology  
ASTM, SC.94 Membership Subcommittee, Nuclear Technology and Applications

**J.K. Langland**

Chairman, NIST Electronics Storeroom Committee

**R.M. Lindstrom**

National Steering Committee for the Advanced Neutron Source  
NIST Ionizing Radiation Safety Committee  
NIST Reactor Safety Evaluation Committee

**J.D. Messman**

Chairman, SAS Audit Committee  
SAS Tellers Committee  
ASTM, E013 Molecular Spectroscopy  
ASTM, SC.01 UV/Vis Spectrophotometry

**J.R. Moody**

ASTM, D-19 Water  
ASTM, SC.05 Inorganic Constituents in Water  
ACS, C002 Analytical Reagents  
IUPAC, 002 Inorganic Chemistry Division  
IUPAC, SC.02 Isotopic Specific Measurements as References  
IUPAC, C.02.01 Atomic Weights  
Chairman, IUPAC Sub-commission on Isotopic Abundance Measurements  
Chairman, Society for Applied Spectroscopy, Baltimore/Baltimore Section  
CSTL Quality Assurance Committee

**P.A. Pella**

ASTM, E.01 Analytical Chemistry for Metals, Ores, and Related Materials  
ASTM, SC.22 Statistics and Quality Control

**K.W. Pratt**

ASTM, D-19.05 Inorganic Constituents in Water  
NIST Research Information Center, Division 834 Subject Specialist  
Inorganic Analytical Research Division Seminar Committee  
Inorganic Analytical Research Division High Purity Reagents Committee

**M.L. Salit**

SAS Tellers Committee

**M.V. Smith**

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

**G.C. Turk**

IUPAC, V.4, Commission on Spectrochemical and Other Optical Procedures for Analysis

**T.W. Vetter**

ASTM, E01 Analytical Chemistry for Metals, Ores, and Related Materials  
ASTM, SC.01 Irons, Steels, and Ferroalloys  
ASTM, SC.02 Ores, Concentrates, and Related Metallurgical Materials  
ASTM, WG.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, Jr.**

IUPAC, Subcommittee for Isotopic Abundance Measurements  
IUPAC, Subcommittee on Natural Isotopic Fractionation  
IUPAC, C.02.01, Associate Member, Commission on Atomic Weights and Isotopic Abundances  
Division 834 Lunch Bunch Committee  
Chairman, Division 834 Seminar Committee

**R.L. Watters, Jr.**

Society for Applied Spectroscopy National Nominating Committee  
Federation of Analytical Chemistry & Spectrometry Society Governing Board  
ASTM, E01 Analytical Chemistry for Metals, Ores, and Related Materials  
ASTM, SC.01 Iron, Steel, and Ferroalloys

ASTM, SC.20 Fundamental Practices  
ASTM, SC.22 Statistics and Quality Control, Vice Chairman

**Y.C. Wu**

ASTM, D19 Water  
ASTM, D19.05 Inorganic Constituents in Water  
ASTM, SC.09 Saline and Brackish Waters

**9. Editorships**

**Michael S. Epstein**

Editorial Advisory Board, Journal of Analytical Atomic Spectroscopy  
Column Editor, Journal of Scientific Exploration  
Editor, CSTL Update Newsletter

**Gary W. Kramer**

Editorial Advisory Board, Laboratory Robotics and Automation  
Executive Editor, Intelligent Instruments and Computers  
American Chemical Society, Computer Buyer's Guide

**Peter A. Pella**

News Editor, "X-Ray Spectrometry," an international journal published by John Wiley and Sons, Limited, West Sussex, England

**John C. Travis**  
Editorial Advisory Board, Spectrochimica Acta B

**Gregory C. Turk**  
Editorial Board, Atomic Spectrometry Updates

## **10. Seminars**

**December 8, 1992**

Joseph A. Keena, Texas Instruments, Inc., Dallas, TX, "Neutron Activation Analysis in the Semiconductor Business" (Division Sponsor: E.A. Mackey)

**December 14, 1992**

William Chang, Materials Science and Engineering Department, University of Southern California, Los Angeles, CA, "Quantitative Evaluation of Curved Diffractor's Properties" (Division Sponsor: D.F.R. Mildner)

**February 26, 1993**

Robert Michel, University of Connecticut, Department of Chemistry, Storrs, CT, "Atomic Absorption and Laser Excited Atomic Fluorescence in the Graphite Furnace For Ultra Trace Element Determinations." (Division Sponsor: M.S. Epstein)

**February 26, 1993**

Juan Ivaldi, The Perkin-Elmer Corporation, Norwalk, CT, "Analytical Advantages of Coupling Simultaneous Atomic Emission Spectra from the Inductively Coupled Plasma with Multivariate Data Processing." (Division Sponsor: M.L. Salit)

**June 29, 1993**

Peter Bode, Interfaculty Reactor Institute, Delft University of Technology, Delft, Netherlands, "Integrated Quality Assurance & Laboratory Accreditation at the Interfaculty Reactor Institute." (Division Sponsor: R.M. Lindstrom)

**September 9, 1993**

Joseph A. Caruso, University of Cincinnati, Department of Chemistry, Cincinnati, OH, "Chemical Speciation Studies by Chromatography Coupled with Plasma Mass Spectrometry Detection." (Division Sponsor: M.L. Salit)

**September 20, 1993**

James E. Currie, Laboratory Automation Standards Foundation, Groton, MA, "CAALS Communication Specification Development." (Division Sponsor: G.W. Kramer)

**September 22, 1993**

R. Kenneth Marcus, Clemson University, Department of Chemistry, Clemson, SC,  
"Radio Frequency Powered Glow Discharges for Atomic Spectroscopy: Precious Metals  
to Ceramics." (Division Sponsor: M.R. Winchester)

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

**November 18-19, 1992**

CAALS Oversight Board Meeting, National Institute of Standards and Technology,  
Gaithersburg, MD (G.W. Kramer)

**December 2-4, 1992**

CAALS Modularity Workshop, National Institute of Standards and Technology,  
Gaithersburg, MD (G.W. Kramer)

**March 17-19, 1992**

CAALS Modularity Workshop, Los Alamos National Laboratory, Los Alamos, NM  
(G.W. Kramer)

**March 23, 1993**

Spectrographers Committee Meeting, Chemical Analysis of Metals Using Optical  
Emission and X-ray Fluorescence Techniques, National Institute of Standards and  
Technology, Gaithersburg, MD (P. Pella)

**April 14-15, 1993**

Workshop on Technology Requirements for Environmental Management, National  
Institute for Standards and Technology, Gaithersburg, MD (B. Watters)

**May 19-20, 1993**

CAALS Oversight Board Meeting, National Institute of Standards and Technology,  
Gaithersburg, MD (G.W. Kramer)

**July 30, 1993**

Accuracy of Lead Measurements of Paint, Soil, and Dust Samples by Laboratory-based  
X-ray Fluorescence, University of Colorado, Boulder, CO (J. DeVoe)

**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, and the chemical characterization of gaseous mixtures.

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 in which the gases range in concentration from the percent to the parts-per-trillion levels, and in complexity from the single to the multicomponent gas 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 research to provide a unified and coordinated approach for investigating physical and chemical processes that influence chromatographic separations and the use of these separation techniques, in a complementary manner, to separate, detect, and quantify individual organic species in complex natural matrices. A great deal of effort in this Group has continued to focus on investigations of the molecular interactions that occur during chromatographic processes and the design of "tailored" stationary phases for specific applications.

Financial support for the Division's FY93 research programs came from four primary sources: the NIST Congressional appropriation which supported fundamental research and measurement activities in trace organic analytical chemistry and gas metrology (41%); reimbursement for research and measurement activities conducted in support of other Federal Agency programs (30%); research and measurement activities in support of the NIST Standard Reference Materials Program which resulted in the certification of 41 SRM/RMs (21%); other research, measurement and service activities undertaken on a cost reimbursable basis in support of U. S. Industry (8%).

This latter number includes the re-value assignment of 61 SRM gas cylinders submitted to us from 14 different clients.

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.

Other Federal and State Government Agencies continue to be the Division's primary customer base, although interactions with the industrial sector are on the increase. During the past year we were involved in 20 projects from 10 Federal and State Government Agencies. As for the past several years, our two largest Other Agency programs are related to providing analytical measurement quality assurance support for (1) epidemiological studies and cancer chemoprevention trials conducted by the National Cancer Institute (NCI) and (2) marine monitoring pollution 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 increased. In addition to providing laboratory based activities and consultations regarding measurement QA, this interaction also involved research concerning the development of miniaturized flow-injection immunoassay, optical planar waveguide devices and supercritical fluid extraction technology for possible use during on-site industrial inspections.

In 1985, when the NCI program began, interlaboratory variability for the measurement of fat-soluble vitamins and carotenoid compounds in serum exceeded 50%. Even short-term intralaboratory repeatability of measurements exceeded 10%, calling into serious question any purported correlations between preventive agent serum concentration and cancer prevention. NIST research and QA activities have fostered a five-fold improvement in interlaboratory measurement precision over the past seven years making it much more feasible to pool and compare data among epidemiological investigations and monitor the course of cancer chemoprevention trials. Interlaboratory precision is approximately 10% and both long and short term intralaboratory precision is less than 5% for participating laboratories. During the past year, in addition to serving as analytical measurement consultants to program participants and

conducting and evaluating data from three interlaboratory studies for fat-soluble vitamins and carotenoid compounds, Division staff have: conducted an interlaboratory study for measurement of ascorbic acid (vitamin C) in serum; provided measurements, using a novel liquid chromatographic stationary phase tailored for separation of carotenoid compounds, to provide QA for algal formulations to be used in NCI trials; analyzed 1500 serum samples for a high-priority study that includes subjects with high susceptibility for contracting cervical cancer; critically evaluated a flow-injection immunoassay system for the determination of estrogen hormones (breast cancer markers) in body fluids; developed a gas chromatography/mass spectrometry method for selenium speciation in several yeast pools being considered for study in NCI human trials.

As in the past, a significant portion of our interactions with industry has come via our collaborative activities with an industrial consortium and two professional organizations. The Consortium on Automated Analytical Laboratory Systems (CAALS) is headquartered at NIST and has seven U. S.- based corporations and three Federal Agencies as members. Research efforts within the consortium are focused on the production of U. S. industry-wide automation compatible systems for chemical analysis. The College of American Pathologists (CAP) is a professional organization 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 FY93 activities were focussed on completion of a definitive method for serum triglycerides, important in coronary heart disease risk assessment. The Motor Vehicle Manufacturers Association (MVMA) is a trade association comprised of seven auto makers with manufacturing facilities in the U.S. The focus of our current program with the MVMA is concerned with the development and issuance of SRMs for measuring gaseous emissions needed to assist in automotive industry compliance with the 1990 "Clean Air Act". Our FY93 activities were directed toward the development of cylinder based gas standards for methanol in nitrogen spanning the 5 to 200 ppm range. Late in FY93 an existing program with California Air Resources Board (CARB) to develop "Clean Air" related cylinder based gas mixture standards was expanded to include the development of a series of reformulated fuel reference materials; the first in the series will be eight "Oxygenates in Gasoline" standards. The Western States Petroleum Association (WSPA) is serving as a co-sponsor for the latter effort. Preliminary efforts were also initiated for development of a 0.25 ppm propane in air SRM requested by the American Industry-Government Environmental Research (AIGER) consortium. The AIGER consortium was formed by the three major U.S. automobile manufacturers and Navistar to represent their industry in the formation of CRADAs with the U. S. government to develop high efficiency-clean cars. The SRM requested will be used by the automakers and EPA to calibrate new instrumentation being developed for monitoring and testing low emission vehicles.



Recent collaborations between Division staff and industrial scientists resulted in the establishment of four new industrial CRADAs in FY93. We worked with the Union Carbide Corporation to develop a proprietary SRM which will be used for providing world-wide quality control of a Carbide commercial product. Researchers in our Analytical Sensors and Automation Group established two new CRADAs with the bioanalytical instrumentation community. A CRADA was established with Photonic Sensor Systems Inc., Atlanta, GA to develop biosensors based on optical integrated chip technology. The objective of the work is to develop highly specific and sensitive chemical sensors for incorporation into hand-held portable units for the detection and/or measurement of chemicals in medical, environmental, industrial, or chemical or biological warfare applications. This joint venture takes advantage of NIST's chemical expertise in biomolecule binding/immobilization and Photonic Sensor System's expertise in optical physics and device fabrication. A CRADA was established with Paraselsian Inc., Ithaca, NY, to develop a new automated immunoassay device for detection and measurement of breast cancer markers in biological fluids. This joint venture takes advantage of NIST's expertise in flow injection immunoassay and biomolecule immobilization technology and Paraselsian's expertise in antibody preparation and purification and instrument design. A new CRADA with Quantec, Inc. is in the process of being established to investigate the development of field-portable surface plasmon resonance devices with antibody-based detection of environmental toxins.

Researchers in the Separation Science Group established a CRADA with CEM Corporation to develop procedures for the organic solvent extraction of contaminants from environmental matrices using microwave heating technology. The objective of the collaborative research program is to develop cost effective and environmentally-friendly methods for extraction of environmental pollutants such as polycyclic aromatic hydrocarbons (PAHs), pesticides/herbicides, and polychlorinated biphenyls (PCBs) from matrices such as soil, air particulate matter, and biological tissues using microwave heating technology. Microwave-assisted extraction procedures offer the potential advantage of more rapid extractions using smaller volumes of hazardous organic solvents than conventional procedures. In this joint venture, the CEM corporation provided hardware and a Research Associate with expertise in microwave technology to work with NIST researchers experienced in the measurement of environmental pollutants.

In FY93 measurement activities within the Division contributed to the development or maintenance of approximately 41 SRMs/RMs including both simple and multicomponent cylinder gas mixtures, permeation devices for NO<sub>2</sub> and SO<sub>2</sub>, clinically and nutritionally significant constituents in human serum and foods, drugs of abuse in both hair and urine, and both chromatographic calibration solutions and soil, sediment and tissue matrices for organic environmental pollutants. An additional 61 SRM gas cylinders were re-value assigned for industrial and other Federal Agency clients.

Two new NIST standards programs were established, in partnership with EPA and Specialty Gas Companies, 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 programs were officially introduced and discussed at the 1993 Pittsburgh Conference in

Atlanta, GA. The first and larger of the two is NIST Traceable (Gas) Reference Materials (NTRMs). NTRMs are being produced and distributed by Specialty Gas Companies with NIST oversight of their production and analysis. Specialty Gas Companies are allowed to develop NTRMs for any pollutant, concentration and balance gas combination for which an NIST SRM suite currently exists. The new program requires that commercial suppliers of gas standards produce candidate NTRM cylinders in batches, 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. Concentration value assignment is based either on comparison to, or interpolation between existing SRMs. Two companies participated in the program in FY93 and produced eight NTRM batches. Three companies have committed to produce a total of 34 NTRM batches in FY94.

The second new program allows Specialty Gas Companies to conduct collaborative research with NIST to develop NIST traceable gas mixtures where no SRM suite currently exists. In FY93, we signed a CRADA with one Specialty Gas Company to develop a suite of ethanol in nitrogen Research Gas Mixtures (RGMs). We are currently negotiating with a second company to develop an RGM for moisture in nitrogen. This effort will require a collaborative effort between the Specialty Gas Company, our Gas Metrology Group and the Process Sensing Group in the Process Measurements Division.

We plan to commence several new projects in FY94. A small portion of our efforts in chromatography and spectroscopy will be redirected toward the general area of real-time and/or in-field analytical measurement technology. Our effort in chemometrically directed multidimensional GC showed promise in FY93 and will be continued in FY94, and our efforts in tunable diode laser spectroscopy will be focused on the measurement of oxygenated hydrocarbons in automotive exhaust in collaboration with the AIGER. FT Raman spectroscopy will also be evaluated as an alternative/complement to Near Infrared and FT-IR spectroscopy for process analytical measurements. The determination of oxygenates in gasoline will be used as a test case. Our efforts in optical planar waveguide sensor technology will be directed toward mixed waste measurements and our flow-injection immunoassay research will be directed toward multianalyte measurements. These new or expanded programs are in response to requests from the process analytical chemistry, health and environmental measurements communities. Other high-priority research areas for the coming year are 1) electrospray ionization of large molecules and 2) sol-gel bonding chemistry for attachment of biomolecules to surfaces. Gaining a clearer understanding of the factors that affect the electrospray ionization process for large molecules will provide us with a new and powerful tool for the characterization and measurement of biomolecules. The lack of adequate bonding chemistries for producing robust and hydrolytically stable, covalent linkages of biologically active molecules to glass surfaces has been identified by representatives of 30 leading U. S. biotechnology companies as one of the top three problems limiting the development and marketability of commercial biosensors.

The overall strength of Division research and service efforts were bolstered by several non-full time permanent staff: three NRC Postdoctoral Research Associates (David Bunk, who contributed to our development of electrospray mass spectrometry methods for determining biomolecule conformation; Janet Morrison, who investigated the application of supercritical fluid extraction technology and capillary electrophoresis to forensic analyses; Steven Page, who investigated the properties of supercritical fluids pertinent to chromatographic separation and extraction); three Research Associates (Dr. Polly Ellerbe and Ms. Susan Tai from the CAP; Dr. Lois Jassie from the CEM Corp.); five visiting scientists and six student appointees.

During the past year, three Division scientists received special recognition for their efforts: Ms. Laurie Brown and Dr. Steven Choquette received the FY93 NIST Applied Research Award for their outstanding efforts and unusual creativity in the conceptualization, development and critical evaluation of an automated Flow Injection Immunoassay device for measurement of breast cancer markers in human serum. Dr. Michele Schantz received an SRMP Measurement Services Award for her outstanding efforts in the development and implementation of analytical methods for the measurement of trace-level organic pollutants for the certification of several natural matrix marine environmental SRMs. In addition, Dr. Willie E. May was elected as the first President of the International Society of Polycyclic Aromatic Compounds.

As stated previously, scientists in the Division are making significant contributions to the development, theoretical understanding and application of new and emerging chemical measurement technologies. 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. The Technical Highlights that follow provide details that reflect the high quality and broad impact of these and other technical activities within the Division.

**B. Selected Technical Reports  
(Organic Analytical Research Division)**

**1. Multianalyte Detection in Flow Injection ImmunoAnalysis (FIIA): Measurement of Estrogen Metabolites for Early Assessment of Breast Cancer Risk**

**L. Locascio-Brown and S.J. Choquette**

Previous automated continuous flow analytical systems employing immobilized immunoreagents have combined rapid, single analyte measurement capability with high sensitivity and accuracy. The selectivity and sensitivity of the detection scheme are inherent to the assay, utilizing antibodies with low cross reactivity to competing chemical species and high affinities to push detection limits of the method. Employing immunoreactive liposomes containing encapsulated or membrane-associated dyes provides high signal amplification in the solid-phase immunoassay. In the past year, efforts in this area have been focussed on the determination of estrogen metabolites by FIIA for early detection of breast cancer. Cancer researchers have shown that the onset of breast cancer is marked by an obvious change in the metabolic pathway of the primary estrogen, 17- $\beta$ -estradiol. Providing an inexpensive and potentially noninvasive test for frequent monitoring of 17- $\beta$ -estradiol and some of the minor metabolites over the course of a lifetime could provide an early indication of the presence of the disease.

The goal of our research over the past year was to develop a prototype assay system for the determination of 17- $\beta$ -estradiol as a test-bed for the measurement of all estrogen metabolites. Normal serum concentrations of estrogens range from 200 pM for serum 17- $\beta$ -estradiol to the low picomolar levels for the minor metabolic products. A competitive, solid-phase immunoassay was performed using a packed column containing the immobilized antigen, and liposomes coated with a high affinity monoclonal antibody. The assay sensitivity was adequate for the serum-based measurements of all estrogen metabolites. We also determined that the detection limits of the method could easily be enhanced by reducing the column length since this parameter is directly related to the amount of immobilized binding sites. Further experiments will be done to determine the feasibility of measuring metabolites at the low levels present in urine, to produce a truly noninvasive technique. Studies are also currently being conducted to extend the method to the simultaneous detection of multiple estrogen metabolites in the same time required for a single analyte. In the modified method, the immunoreactor column contains two or three immobilized estrogen metabolites. Different encapsulated or membrane dyes are incorporated into the liposome structure to indicate each separate analyte. Initial experiments are being done to determine 17- $\beta$ -estradiol and estrone by this technique.

A FIIA system has also been designed for the measurement of chemical/biological warfare agents, as part of a project sponsored by the U.S. Army Edgewood Research and Development Engineering Command (ERDEC). The assay system for measurement of ricin, a very potent biological agent, uses the same polyclonal antibody immobilized in the column and onto the

liposome surface. The polyclonal antibodies can bind to several antigenic sites on the ricin protein; therefore, ricin-bound to liposomes will subsequently bind to the immobilized sites. This assay format was chosen to minimize the handling of the toxic protein during system development and operation since none of the supplied reagents are prederivatized with the toxin. Miniaturized FIIA systems based on microfabrication techniques are being designed in an effort to develop field-portable devices for military and environmental applications.

## 2. Optical Waveguide Interferometric Immunosensors

S.J. Choquette and L. Locascio-Brown

Phase-sensitive optical waveguide biosensors offer an attractive alternative to the more commonly implemented fluorescence techniques. There are several advantages to using an interferometric assay for biosensing: (1) common mode interferences, such as nonspecific adsorption, are eliminated by a dual beam design; (2) inexpensive telecommunications fiber or planar waveguides may be used; and (3) inexpensive and rugged silicon photodiode detectors replace photomultipliers and monochromators. For these reasons, over the last several years we have investigated the development of biosensors based on the use of optical waveguide interferometers.

Our initial work, as reported in last year's technical highlights, focussed on the development of an all fiber-optic Mach Zehnder interferometer for a thermal immunoassay. Because of low protein coverage on the surface of the fiber, the sensitivity and reproducibility of these measurements was limited. In order to increase the amount of active protein available for the assay, the sensing fiber was placed into an analytical column containing the immobilized antibodies. Although the sensitivity was enhanced, thermal noise increased as a result of locating the reference fiber outside of the flow cell and, negated any advantage to this approach. We are continuing to study the use of a thermal immunoassay with a coupled enzyme system immobilized directly to the sensing fiber. We anticipate that the reduction of oxygen production (bubbles) and the additional enthalpic response will help to increase sensitivity, without additional background noise.

In addition, we will investigate the use of fiber optic and planar waveguide evanescent wave interferometers for immunosensing applications. For the fiber implementation, we are currently fabricating and studying the phase response of a polished fiber field access coupler. This device is expected to yield a rugged and moderately sensitive device based on currently available telecommunications devices. The planar waveguide implementation will rely on the use of custom designed silicon nitride waveguides, currently used in our attenuation based immunoassays. Because these devices have a high refractive index, increased sensitivity to refractive index perturbations is expected (over fiber based devices). Both systems will initially use our previously designed diode array detection scheme to detect fringe shifts. This, however, will be replaced by a single diode to increase durability, compactness, and reduce cost.

### 3. Detection of Organic Residues from Gunpowder Firings

W.A. MacCrehan

In the past year, OARD has reinitiated the effort to develop new technology for the investigation of handgun and explosive crimes based on organic residue analysis. Past NIST work showed that Micellar Electrokinetic Capillary Electrophoresis (MECE) is a potentially powerful measurement approach for the detection and identification of the organic traces that remain after the firing of gunpowder and explosives. Detectable compounds include nitro- aromatic and aliphatic primers and propellants, aromatic amine stabilizers, phthalate plasticizers and perhaps decomposition products. The predominantly neutral compounds are separated in the high electric field by the addition of a charged micellar agent to the capillary buffer. The detergent micelles migrate at a rate that differs from the aqueous electrolyte, creating a pseudostationary phase. Analyte partitioning retards their migration in a manner similar to reverse-phase LC. The technique is ideal for forensic work because it provides high resolution, rapid analysis time and uses very small sample sizes.

Although we previously demonstrated the ability of MECE to detect residue particles immediately following test handgun firings, more research will be needed to successfully apply this technology to forensic casework. We have established a collaborative effort to further develop the MECE technique with a well-known trace evidence researcher and expert witness from George Washington University's Forensic Science Department, Professor Walter Rowe, to bring MECE technology closer to the commercialization and routine casework stage. We are currently addressing issues of measurement reproducibility and quantitative extraction of the organic constituents from the residue particles. In this coming year, we hope to develop sampling materials and protocols, determine the effect of the time and exposure on the evidence, and validate the MECE technique against the existing metals-based tests.

### 4. Measurement Uncertainty and Its Propagation in 1-D Gel Electrophoresis

D.L. Duewer and D.J. Reeder (831)

Determinations of the molecular weight ("size") of biomolecules often rely on electrophoretic separation and calibration against known standards. Protein and DNA typing in medical, paternity, and forensic applications often are accomplished in this manner. When results need to be compared among laboratories over space or time, knowledge of measurement uncertainties is crucial.

In collaboration with the FBI's Forensic Science Research and Training Center and NIST's Statistical Engineering Department, we are completing the analysis of a large interlaboratory comparison study on DNA restriction fragment length polymorphism (RFLP). The forensic utility of this DNA profiling technology for identifying serial felons is critically dependent upon

knowledge of the expected measurement uncertainty. Most of the overall RFLP interlaboratory measurement variance is attributable to electrophoretic process variation and small but systematic protocol differences among laboratories. Variance arising from post-electrophoresis autoradiogram imaging processes is a generally minor component, but it sets a lower limit to the variance of quantitative gel electrophoretic measurements and is clearly a complex function of fragment size.

Using the results and the autoradiographic images of the interlaboratory study, we have demonstrated that variability in the RFLP measurement process can be described as a 0.2 - 0.4% variation in the measurement of the relative position of sample and calibration band centroids. Interlaboratory replicate measurements for a given band on a given autoradiogram show only about 0.1% variation. Absolute protocol standardization has a 0.1 to 0.2% variation. Thus, perhaps only a two-fold improvement could be achieved from further interlaboratory protocol standardization without fundamental changes to the measurement system.

The functional form relating interlaboratory sizing variance to DNA fragment size is complex. It can be modeled from a sigmoidal calibration function, modulated by nonuniform uncertainty in the measurement of the fragment electrophoretic migration distance through the gel. We have shown that all recent interlaboratory forensic profiling results from North America and from Europe are remarkably well described by this model. We believe that the general form of our results has general applicability to other biomolecule measurement systems.

## **5. Multidimensional Chemometric Chromatography**

**S.N. Chesler and D.L. Duewer**

A major focus of modern analytical science has been directed toward achieving higher chromatographic resolution for characterizing complex mixtures. Unfortunately, increasing chromatographic resolution generally increases the time required per analysis. Inspired by the automotive industry's need for rapid characterization of engine exhaust streams (140+ analytes of regulatory interest), we are investigating ways of dramatically decreasing analysis time without sacrificing analysis quality.

Building upon recently developed chemometric analysis concepts, we seek to reduce chromatographic analysis time through use of a lower resolution system coupled to multidimensional signal analysis. Spectroscopic detection systems can provide multivariate signals for a single column, but are generally slow, insensitive, and expensive relative to the best available univariate detectors. We are currently investigating the utility of combining univariate detector signals obtained from multiple columns of differing separation principles and temperatures.

We are modeling an ideal device using a commercial dual-column gas chromatograph, and simulating a real complex sample with well behaved, non-toxic mixtures of pure materials. In routine chromatographic analysis practice, quantitative results depend upon efficient peak recognition, integration, and approximate deconvolution but are relatively insensitive to run-to-run variation in analyte elution time. In contrast, multivariate chemometric analysis does not perceive independent peaks but does require that intensity and time information in the signal for a given sample on a given column/temperature must be transformable to a stable representation. We have demonstrated that: (1) external, between-sample standardization is not sufficient to achieve separation-axis (time) stability and (2) internal standardization using just three peaks per individual column/temperature is sufficient. In collaboration with Professor Donald Dahlberg, Lebanon Valley College, we have developed MATLAB® software for appropriately standardizing raw chromatographic signals. We are currently defining a model sample to challenge the various available multivariate quantitative analysis software systems, including: classical least squares (CLS), principle component analysis (PCA), partial least squares (PLS), and artificial neural networks (ANN). During the coming year we expect to complete evaluation of these approaches, document our results in an archival form, and extend the model hardware and chemometric analysis methods to more challenging samples.

## 6. Evaluation of Fluid Phase Behavior in Supercritical Fluid Chromatography and Extraction

S.H. Page, J.M. Morrison, S.J. Choquette and R.G. Christensen

Conventional extraction methods that use organic solvent to extract or separate polar or high molecular weight analytes from a matrix are generally time consuming and produce large amounts of hazardous waste. Supercritical fluids (fluids with gas and liquid-like properties) can greatly minimize solvent consumption and greatly reduce the amount of hazardous waste generated. This is important because concerns about the use of chlorinated solvents have recently been debated. In addition, extractions with supercritical fluids are extremely fast as compared to conventional liquid extraction techniques. Supercritical fluid technology can help industry maintain their competitiveness while phasing out the use of hazardous solvents. However, important properties such as the phase behavior of mixtures are lacking for many of the supercritical fluids. Previous methods to investigate phase behavior were very labor intensive because they required continual visual monitoring of the fluid by a technician or they required subsequent chemical or spectroscopic analysis of samples carefully withdrawn from the gas and liquid phases present in a chamber.

In response to the need to understand phase behavior, we have developed an extremely fast and reliable technique to monitor the phase behavior of mixtures and to determine the conditions of the supercritical fluid region. The method utilizes laser light scattering to observe the phase behavior of the fluid. When a fluid in the near critical region undergoes a phase transition, liquid droplets or gas bubbles are evolved. Abrupt signal changes in the laser light, after it has



passed through the fluid, indicate that the laser light has been scattered by the bubbles or droplets; a phase transition has occurred. Because phase separations are dependent upon pressure (p), temperature (T), and the components of the mixture (x), our system enables rapid screening of many combinations of p-T-x to determine the conditions of the supercritical fluid region. We have greatly minimized the cost of the system components by eliminating the need for custom machined parts and by replacing the optics with optical fibers. Also, the capability to completely automate the system has been preserved.

We have demonstrated the reliability of the technique by rapidly screening 18 CFC (chlorofluorohydrocarbons) and carbon dioxide based fluids. These fluids were used to extract cocaine from hair as part of a drug screening procedure for drugs of abuse. Our results were used to help replace the CFCs with carbon dioxide. In this case, potentially ozone depleting compounds (CFCs) were successfully replaced with a more environmentally compatible compound without diminishing the quality of the extraction procedure for trace levels of drugs.

## 7. Supercritical Fluid Extraction (SFE) of Trace Organic Species from Natural Matrices

B.A. Benner, Jr., J.F. Morrison, and S.H. Page

In the last ten years, supercritical fluid extraction (SFE) has emerged as an alternative extraction technique to conventional liquid solvents for some sample matrices. The benefits of "gas-like" diffusivities and "liquid-like" solvation of supercritical fluids have yielded faster and more complete extractions of specific analytes (e.g., hydrocarbons) from specific samples (e.g., soils). Despite the potential advantages of supercritical fluids as extractants, growth and acceptance of SFE as a routine and reliable sample preparation method has been hampered by the limited understanding of the mechanisms that control SFE processes and the factors, both physical and chemical, that affect extractability of target analytes from sample matrices. During the past year, we have worked in a number of different areas involving SFE of environmentally and clinically relevant analytes from various matrices. Studies have been undertaken to gain an understanding of the interactions that occur among the analytes, the matrix surface, and supercritical fluids, as well as the mechanisms and kinetics that control these interactions.

Work has continued in optimizing the extraction efficiencies of polycyclic aromatic hydrocarbons (PAHs) from a number of natural matrix Standard Reference Materials (SRMs) including SRMs 1649 (Urban Dust/Organics), 1941 (Organics in Marine Sediment) and 1650 (Diesel Particulate Matter). Previously, it was shown that supercritical chlorodifluoromethane (R22) yielded good extraction recoveries for PAHs from SRM 1649. Results for SRMs 1941 and 1650 were less favorable, with less than quantitative recoveries for the higher molecular weight PAHs (MW  $\geq$  252 amu). Recently, comparable results to those generated using R22 for the SFE of SRM 1649 were achieved with the more "environmentally-friendly" CO<sub>2</sub> at 200 °C, corroborating data published by other workers [Hawthorne et. al., Anal. Chem. 64, 1614-1622 (1992)]. The improvements in the extraction efficiencies for CO<sub>2</sub> at the higher temperature (T<sub>c</sub> = 31 °C) are

based on more favorable kinetics. Continued difficulties in obtaining quantitative SFE for SRMs 1941 and 1650, even when using high temperature CO<sub>2</sub>, suggest that some matrices require binary (or ternary) fluid mixtures for complete extraction.

We observed reproducible restrictor plugging when performing SFE of SRM 1649 with CO<sub>2</sub> at 200 °C. Chemical (GC/MS and Direct Insertion Probe-MS), spectrometric (IR and Raman microscopes and X-ray fluorescence), and microscopic (light and scanning electron microscopes) techniques were used to identify the components of these plugs. This appears to be the first known study to characterize the material causing the blockage of a restrictor in SFE.

On-line SFE/GC/MS has been used in our laboratory to exploit the sensitivity of the technique in those cases where sample size is limited. After SFE, the extracts are trapped directly on a cryogenically-cooled retention gap prior to GC/MS analysis. Experiments with microgram quantities of some SRMs and hair samples suggest that this technique may be valuable as a semi-quantitative screening tool for identifying trace and compositional materials associated with samples of environmental, clinical and forensic significance.

Studies are currently underway in our laboratory to evaluate SFE as an alternative method for the isolation of drugs of abuse from human hair. A variety of supercritical fluid-modifier combinations have been investigated for the recovery of cocaine from spikes on filter paper, teflon wool, and powdered and segmented hair, as well as from drug-fortified hair. These experiments allowed the optimization of extraction conditions and additionally provided an opportunity to study the influence of the matrix on extractability of cocaine.

The most efficient recoveries of cocaine from fortified hair and from filter paper were obtained using CO<sub>2</sub> modified with water/triethylamine (TEA) or with methanol/water/TEA; CO<sub>2</sub> alone was inefficient at extracting cocaine from these matrices (< 5% recoveries). Preliminary experimental evidence suggests that triethylamine displaces cocaine from adsorptive matrix sites, thereby making the drug available for extraction. Using CO<sub>2</sub>/water/TEA, SFE recoveries of cocaine from fortified hair were about 90% relative to acid extraction followed by solid phase extraction. The total time for SFE and subsequent chromatographic analysis was approximately 2 hours, compared to 24 to 28 hours for the acid extraction procedure. Further experiments have demonstrated the feasibility of performing a pre-cleaning step with pure CO<sub>2</sub> for the selective removal of natural oils, waxes, and other interferences from hair prior to extraction with the modified fluids.

## 8. Commercialization of Liquid Chromatographic Phase Engineered for Separation of Carotenoid Compounds

L.C. Sander, N.E. Craft, K.S. Sharpless, and S.A. Wise

As part of an ongoing research effort to understand and utilize molecular interactions that provide for separations in liquid chromatography, the Separation Science Group has developed new stationary phases optimized for the separation of carotenoid isomers. Carotenoids are a class of organic compounds that occur naturally in fruits and vegetables and are beginning to be of significant interest in a variety of industrial and health fields. Carotenoids are used widely as natural pigments, as nutrients in food, and are being investigated for their effect in the reduction of various diseases including cancer. Subtle differences in the geometry of carotenoid molecules give rise to numerous isomers and related compounds, making the separation and measurement of individual carotenoid species very difficult. For example,  $\beta$ -carotene is being used as a food additive for its perceived health value and is being investigated by the National Cancer Institute for its cancer preventative properties in several epidemiologic studies and chemoprevention trials. However, the results of these studies are often confounded by the inability to measure individual molecular species. Because of the economic and medicinal significance of these compounds, the ability to separate individual carotenoid compounds is of considerable importance.

The ability to separate and measure carotenoids has been enhanced recently by the development of a new stationary phase for liquid chromatography tailored specifically to "recognize" the subtle structural variations among these compounds. To a large extent, the ability of a column to provide separation is controlled by the structure of the bonded phase at the molecular level. The selection of suitable substrate properties (particle size, pore size, and surface area) and surface modification procedures (ligand and phase type) permits wide variations to be created in the retention properties of the resulting bonded stationary phase. By optimizing each of these parameters for carotenoids, a column was developed which provides significantly improved separations of complex isomer mixtures. This column utilizes an unusual silica substrate with moderate pore size and moderate surface area ( $\sim 200 \text{ \AA}$  pore diameter,  $\sim 200 \text{ m}^2/\text{g}$  surface area), in conjunction with polymeric  $\text{C}_{30}$  surface modification chemistry. This combination of properties results in a column with high absolute retention and enhanced shape selectivity towards carotenoid isomers, properties that are not available with current commercial columns.

The development of a carotenoid column represents a practical application of years of basic research into the fundamental nature of chromatographic retention processes. Several manufacturers of chromatographic instrumentation have expressed interest in this unique column technology. We are currently working with one of these manufacturers (YMC, Inc., Wilmington, NC) to transfer this column technology to the private sector. The commercial availability of this "carotenoid column" will enable significantly improved measurements of carotenoids to be made on a routine basis.

## 9. Carotenoid Measurements Applied to Cancer Risk Assessment

K.S. Sharpless and N.E. Craft

Epidemiologists have observed a reduced incidence of lung cancer in people who have an elevated intake of fruits and vegetables. Epidemiologic studies also suggest that eating fruits and vegetables may reduce the risk of other cancers as well. Because low serum levels of  $\beta$ -carotene are associated with the subsequent development of lung cancer,  $\beta$ -carotene may be the protective factor present in the fruits and vegetables. However, the lowered risk of cancer may be due to other carotenoids (or other components) that are present in the fruits and vegetables and are ingested along with the  $\beta$ -carotene. Until recently, analytical methods for carotenoid measurements have focused primarily on the measurement of  $\beta$ -carotene, and the importance of these other carotenoids has not been studied adequately.

We have developed a liquid chromatographic (LC) method that is capable of measuring lutein, zeaxanthin, and  $\beta$ -cryptoxanthin, along with *cis*- and *trans*-isomers of lycopene and  $\alpha$ - and  $\beta$ -carotene. Retinol (vitamin A) and retinyl palmitate are measured as well. (Using a second detector in series, the method is also able to measure  $\delta$ -,  $\gamma$ -, and  $\alpha$ -tocopherol, forms of vitamin E, which may also reduce the risk of various cancers.) The method has a precision of 3 to 5% relative standard deviation over time. At the request of the National Cancer Institute (NCI), this LC method has been applied to the analysis of serum samples from 622 Hawaiian men of Japanese descent and 942 women who have or do not have cervical cancer. These samples are part of two NCI studies to evaluate the possible relationship between serum carotenoid levels and cancer risk.

Levels of individual carotenoids and tocopherols covered a range of two orders of magnitude in both studies. In well-nourished populations, the retinol level in serum is regulated by the liver; retinol in these samples covered a range of about one order of magnitude. The Hawaiian men of Japanese descent consume an atypical "American" diet.  $\beta$ -Carotene had been previously measured in the Hawaiian samples for studies involving lung, colon, rectum, stomach, and bladder cancers. In the current Hawaiian study and the cervical cancer study, we measured the carotenoids, retinoids, and tocopherols listed above. In general,  $\beta$ -cryptoxanthin, a carotenoid found in oranges, papaya, pineapple, guava, and mangoes, was found at higher levels in the Hawaiian samples than are generally observed in serum from mainland American populations. Lycopene, which is found in tomatoes, was lower in the Hawaiian samples than in the general population, and occurred at expected levels in the women in the cervical cancer study. The relationship between specific carotenoid consumption and cancer reduction in these populations is being determined by combining the NIST analytical data with epidemiological data collected by the NCI.

## 10. Evaluation of Novel Phases for GC and SFC Separations of PCB Congeners

B.R. Hillery, M.M. Schantz, and S.A. Wise

Though the use of polychlorinated biphenyls (PCBs) has been banned since the seventies, their chemical stability is such that they remain a ubiquitous environmental pollutant. They are routinely found in marine tissues and sediments. Recent reports indicate that they may also be found in building materials and combustion products. Since PCBs are subject to environmental compartmentalization, PCB congeners released in trace amounts in the environment may bioaccumulate, thus increasing the potential for adverse health effects.

The 5% phenyl methylpolysiloxane stationary phase typically used in the gas chromatographic (GC) separation and determination of PCBs does not have the selectivity necessary to separate all congeners. As part of our continued research into the molecular interactions responsible for separations in the chromatographic process, we have evaluated a series of structurally related stationary phases that show improved selectivity for PCB congener separations. These 25% cyanobiphenyl methylpolysiloxane phases differ primarily in the position and number of the cyano functional group, and they exhibit subtle differences in their selectivity for individual congeners.

These novel phases have been investigated in GC with flame ionization and mass spectrometric detection and in supercritical fluid chromatography (SFC) with electron capture and UV detection. This series of columns has been found to have a greater degree of solute-stationary phase interaction based on molecular geometry than the typical phase. In addition, the new phases exhibit a shape selectivity approaching that of a smectic liquid crystalline phase, i.e., planar, non-ortho substituted congeners have increased retention relative to nonplanar PCB congeners. This shape selectivity is enhanced in SFC, where a planar hexachlorobiphenyl is retained longer than the higher molecular weight hepta to decachlorobiphenyl congeners.

The combined polarity and planarity effects of these phases allow for the separation of PCB 138, PCB 163, and PCB 164, which coelute on the stationary phases typically used for PCB measurements. Among environmental contaminants, PCB 138 is one of the most commonly measured congeners. It has recently been estimated that reported values for PCB 138 may be in error by as much as 30% due to this coelution problem.

Preliminary investigations of marine matrix Standard Reference Materials (SRMs) have shown that PCBs 163 and 164 are also present in the environment. Using these new phases, the concentrations of PCBs 138, 163, and 164 will be measured in SRM 1945 (Organics in Whale Blubber) and SRM 1588 (Organics in Cod Liver Oil) to provide updated information for these congeners in these important marine matrix SRMs.

## 11. Development of an Analytical Method for Determination of Planar PCBs in Environmental Samples

R.M. Parris and L.C. Sander

The quantification of planar polychlorinated biphenyl (PCB) congeners is important both because of their toxicity and the resulting human health implications. These analytes are of interest in several national environmental monitoring programs charged with determining the current status of, and any changes over time in the environmental health of the estuarine and coastal waters of the United States. The most toxic of the PCB congeners are those denoted as planar or "non-ortho" PCBs, which have no ortho-chlorine substituents to the biphenyl link and that also have multiple chlorination at ring positions 3, 4, and 5. The lipophilicity and persistence of these ubiquitous compounds contribute to high bioaccumulation potentials in human tissue and in foods of animal origin.

In environmental samples, the concentration of the planar PCBs is much lower than the concentration of the nonplanar congeners being monitored. Estimates of the concentration of these compounds range from pg/kg (part-per-quadrillion) in human serum to the ng/kg (part-per-trillion) to low  $\mu\text{g}/\text{kg}$  (part-per-billion) concentrations in environmental samples with higher lipid content. Their determination is further complicated because the planar congeners coelute with or are only partially resolved from other congeners with the gas chromatography (GC) methods and columns typically used for PCB determinations.

NIST has been among those laboratories at the forefront of nonplanar PCB congener determinations in environmental samples for a number of years. Appending an additional sample preparation step in which planar and nonplanar PCB congeners are separated using a liquid chromatographic column with a pyrene bonded phase in the normal-phase mode at subambient temperatures has enabled us to also determine the concentrations of selected planar PCBs in these samples. The separation of the planar and nonplanar fractions eliminates coelution of critical PCB pairs and yields a much simpler chromatogram with stable baselines, important in quantification of these low-level species. NIST's enhancement of this step, the use of subambient column temperatures, is of considerable practical significance because it improves this class separation and thus facilitates fraction collection in real samples such as complex environmental materials. Also, this method is one that could be utilized routinely in many laboratories and doesn't require the use of specialized instrumentation such as dual-column GC instrumentation.

The inclusive sample preparation includes a non-aqueous size-exclusion chromatographic step to remove the majority of lipid and biogenic material, which is followed by normal-phase fractionation on an aminopropylsilane column in the normal-phase mode to isolate the PCB-containing fraction. This PCB fraction is then injected onto a bonded pyrene liquid chromatographic column at subambient temperature to isolate the planar from the nonplanar PCBs. This final planar PCB fraction is analyzed using capillary GC with mass spectrometric detection.

This method has been successfully used to determine planar PCBs 77 and 126 in SRM 1588, Organics in Cod Liver Oil, which has certified values for selected nonplanar PCB congeners, chlorinated pesticides and alpha-tocopherol, and is used by the food, health and environmental communities as a high-lipid tissue surrogate. Measurements in other NIST SRMs such as SRM 1945, Whale Blubber, and SRM 1974a, Organics in Mussel Tissue, are planned.

## 12. Protein Molecular Weight Determinations by Electrospray Ionization Mass Spectrometry

**D. Bunk and M.J. Welch**

The structures of proteins are dictated primarily by the amino acid sequences, but agents within a protein's environment can chemically alter its structure. For example, blood proteins such as albumin and hemoglobin can form chemical adducts with certain drugs. Hemoglobin adduction is a clinically valuable indication of tissue exposure, providing information about the effects of drug doses. An important first step to the structural characterization of a protein is determining its molecular weight. An accurate molecular weight can indicate whether a protein possesses its native structure or has been chemically modified; for modified proteins, the molecular weight can give insight into the form of the chemical modification.

An important new tool for the molecular weight determination of proteins is electrospray ionization mass spectrometry (ESI-MS). Prior to the development of ESI-MS, most of the techniques used for the measurement of protein masses had accuracies limited to  $\pm 5-10\%$ . Mass accuracies of  $\pm 0.01\%$  are routinely obtained with ESI-MS for proteins as large as 100 kilodaltons. The analysis can be performed within minutes and requires picomole amounts of sample. In the electrospray ionization process, ionized protein molecules are produced from solution by creating a spray of highly charged droplets in the presence of a strong electric field. The application of a heated dry gas produces rapid solvent evaporation from the droplets, resulting in multiply charged protein ions in the gas phase.

In our molecular weight determination of a human serum albumin (HSA) material, the electrospray mass spectrum indicated two forms of the protein; one observed at mass 66,440 and the other at 66,548 D. The first mass is in excellent agreement with the mass of HSA (66,438 D) calculated from its amino acid sequence. The second form was tentatively identified as a mixed disulfide conjugate of HSA with cysteine; a cysteine-HSA conjugate should be observed 101 D higher than native HSA. Treatment of the HSA sample with a reagent to cleave the disulfide nearly completely eliminated the second HSA form in the ESI mass spectrum, thus supporting this assignment as a cysteine-HSA conjugate.

Large proteins composed of smaller subunits can also be analyzed by ESI-MS. Although electrospray is a gentle ionization technique resulting in little or no fragmentation, noncovalent bonds, such as those connecting the subunits of a large multimeric protein, can be dissociated in the electrospray process. In the electrospray mass spectrum of lactate

dehydrogenase (LDH), a large tetrameric protein with a molecular weight of 144 kD, strong signals were observed for the two different subunits of this protein.

Because the electrospray ionization process begins with the protein sample in solution, ESI-MS can be readily coupled to liquid chromatographic methods of separations. In particular, the microscale separations of capillary reverse phase liquid chromatography coupled to ESI-MS produces a sensitive and accurate method for molecular weight determination of complex mixtures of proteins or proteins in complex matrices like serum. By combining these two techniques, the resolution limitations of both are diminished, allowing the analysis of minor protein components in a complex sample. In FY94, we plan to evaluate capillary HPLC-ESI-MS for the identification and quantitation of serum albumin and other clinically relevant proteins.

### 13. The Development of a Definitive Method for Serum Triglycerides

P. Ellerbe and L.T. Sniegoski

While the measurement of triglycerides (TG) in serum has always been an important clinical measurement because of the correlation between high levels of TG and the risk of heart attack or stroke, the accuracy and precision required for that particular purpose were low. However, medical researchers found that the total level of cholesterol in blood was not as important a marker for risk of heart disease as the levels of cholesterol associated with the low density lipoproteins (LDL) and the high density lipoproteins (HDL) in blood. The level of HDL-cholesterol may be determined directly, whereas the LDL-cholesterol cannot be determined by routine clinical methods. Instead, the LDL value is calculated from a formula that uses the measured values for total- and HDL-cholesterol and TG. Thus, accurate calculation of this important risk factor depends upon accurate determination of the TG value.

To provide an accuracy base for TG, NIST, in cooperation with the College of American Pathologists (CAP) in a long-standing program, has developed a definitive method that actually consists of two separate assays, as desired by the clinical community: total glycerides consisting of the total tri-, di-, and monoglycerides plus free glycerol; and triglycerides only. The latter assay involves an extra chromatography step to separate the triglycerides from the other glycerol-containing species.

Definitive methods for organic analytes in serum are based upon the technique of isotope dilution/gas chromatography/mass spectrometry because it does not depend on sample recovery, can provide high precision, and can be tested for bias. Our methods use a specially modified mass spectrometer for high precision ion abundance measurements and a measurement protocol which brackets samples both in time and weight ratio. To reduce the chances of bias introduced by weighing errors, we cross-check independently prepared calibration standards and we measure multiple sets of samples. Bias in the measurements is tested for by remeasuring samples using a different GC column, a different pair of ions, and/or a different method of ionization. If there



are no significant differences from the original values, it is strong evidence for no significant bias in the measurements.

The method has now been thoroughly tested on lyophilized, frozen, and fresh serum. For example, analysis of a lyophilized serum pool from the CAP found the mean total glycerides to be 166.10 mg/dL, with a relative standard error of the mean of 0.34%; and the mean triglycerides only to be 139.10 mg/dL, with a relative standard error of the mean of 0.11%. When samples were remeasured as described above, the differences from the principal measurement were 0.10% for measurement with a different pair of ions on a different GC column, and 0.31% for measurement by methane CI, thus indicating that the bias is not significant. The results demonstrate that the method is worthy of consideration as a Candidate Definitive Method.

The method will be used to certify SRMs, to validate the reference method developed by the Centers for Disease Control, and to value assign CAP proficiency testing Survey materials.

#### 14. Selenium Speciation in Yeast in Support of Cancer Chemoprevention Trials

M.J. Welch and E. White V

High selenium yeast is presently being tested in cancer chemoprevention trials being conducted by the National Cancer Institute (NCI). The active component is thought to be the selenium present in amino acids which are synthesized and incorporated into protein when yeast is grown in a medium rich in inorganic selenium. The major selenium containing amino acid observed in yeast is selenomethionine, but selenocystine has also been reported, and low levels of the selenium analogs of other naturally occurring sulfur compounds seem likely to be present. NCI requested the determination of selenomethionine in two dried yeast samples being used to dose subjects in ongoing cancer prevention trials.

There are no generally accepted methods for the determination of selenomethionine. The two most promising methods were protein hydrolysis followed by analysis of the digest for selenomethionine and determination of methylseleno groups in the yeast by conversion of these to methyl selenocyanate with cyanogen bromide followed by determination of the methyl selenocyanate. The hydrolysis procedure is specific for selenomethionine whereas the cyanogen bromide method is subject to interference from other compounds containing the methylseleno group.

The use of protein hydrolysis in methods for detection of selenomethionine in various materials, including yeast, has been reported in the literature, but partial destruction of this amino acid was noted in some cases. Several attempts at acid hydrolysis under conventional conditions (with the exclusion of oxygen), followed by sample clean-up, derivatization, and analysis by gas chromatography/mass spectrometry (GC/MS) gave widely scattered values for the

selenomethionine concentration. These values were always much lower than those from the cyanogen bromide method. If this method is to produce quantitative results extensive investigation of the hydrolysis conditions will be required.

The conversion of methylseleno groups to methyl selenocyanate with cyanogen bromide followed by determination of the selenium in the product by a variety of analytical techniques has also been reported. These methods have been applied to a number of matrices including yeast. Although no compounds with methylseleno groups, other than selenomethionine, are known to occur in yeast, the possibility cannot be excluded. Analysis of the two NCI samples by reaction of the yeast with aqueous cyanogen bromide in the presence of stannous chloride to prevent oxidation, followed by determination of the methyl selenocyanate by GC/MS gave selenomethionine concentrations of 700 and 1390  $\mu\text{g/g}$  of yeast with estimated CV's of about 10%. These values indicate that about 45% and 47%, respectively, of the total selenium in the samples, as measured by neutron activation, is present as selenomethionine.

## 15. Summary of Interlaboratory Studies Concerning the Determination of Drugs of Abuse in Hair

L.T. Sniegowski and M.J. Welch

The analysis of hair for drugs of abuse is a promising alternative to urine drug testing. Hair can provide a long-term history of drug use, in contrast to urine, which only provides information about drug use over the previous 48-72 hours. In addition, samples can be collected from the scalp of most individuals without embarrassment and with no cosmetic effects. As part of a research program to investigate analytical aspects of hair analysis through an interagency agreement with the National Institute on Drug Abuse (NIDA), NIST is conducting interlaboratory studies to determine the strengths and weaknesses of methodologies used for hair analysis for drugs of abuse and to determine possible cutoff levels for drugs of abuse in hair. Participating laboratories are sent hair samples for analysis by their methods. NIST compiles the results and informs each participant how their results compared with the overall results.

To date, three exercises have been completed. The number of laboratories participating has increased steadily, with 7, 10, and 13 laboratories sending in results for exercises 1, 2, and 3, respectively. These laboratories include private U.S. companies involved in drug testing, local government laboratories from around the U.S., and research institutions from the U.S. and Europe.

The findings have been that generally laboratories perform well at identifying which drugs are in hair, but that quantitative results vary considerably. Various extraction approaches have been used to remove the drugs from the hair for analysis. Results are not clearly better for any one approach; results depend more on how carefully extractions are performed and the amount of time allowed for the extractions. GC/MS is the preferred technique for measuring the extracts,

although laboratories using MS/MS on hair extracts, with or without GC, have generally produced acceptable results. The only approach tried to date that was clearly unacceptable involved direct probe MS/MS analysis of intact hair (no extraction). Results from this approach were by far the worst, both qualitatively and quantitatively, of any reported. Another finding is that hair that has been soaked in solutions of drugs, by the approach that we have used, is not always a good substitute for drug users' hair. Some laboratories use washing procedures that includes analysis of the washes for drugs. These laboratories detect differences between the soaked and the drug users' hair. We are investigating alternative soaking procedures to better mimic drug users' hair.

A one-day workshop was held at NIST for participants in the studies. Several talks were presented on new measurement methods and research related to hair analysis for drugs of abuse including one describing a new NIST developed method for extracting drugs of abuse from hair using doped supercritical CO<sub>2</sub>. Discussions were also held on plans for future interlaboratory exercises.

#### 16. Bilateral Comparison of Primary Gas Standards with the Netherlands Measurement Institute (NMI)

W.D. Dorko, G.D. Mitchell, and A. Alink (NBI, the Netherlands)

Current trends in the area of exchanging goods and services across international borders has increased the awareness of needs for traceable standards. Presently, each country has its own regulatory need for traceable standards. If a traceability link could be established across international boundaries, then measurements in each country would be comparable. Then, if issues of international trade are resolved, companies who do business across international boundaries would not have to repeat costly chemical measurements. The question being asked now is: Would chemical measurements made in Europe, using European standards, compare with measurements made in the U.S. using U.S. standards?

To answer that question, NIST and the Measurement Institute of the Netherlands (NMI) have agreed to exchange gas mixture samples for mutual analyses so that the two institutes could begin to study international measurement intercomparability. NIST produces Standard Reference Materials, which are recognized within the U.S. and internationally, while NMI produces Primary Reference Materials which are recognized in Europe. If we can show comparability between our standards and NMI's standards, traceability links could be established *scientifically*. Then future trade agreements could reach a definition of traceability that would satisfy *political* entities.

During the past year, NMI prepared six gas mixture standards in high pressure metal cylinders by their primary method, which is gravimetry, and sent them to NIST. The Gas Metrology

Group of NIST used appropriate instrumental analytical techniques to compare the concentration of the analytes within the mixtures to NIST developed primary standards.

The first two mixtures were carbon monoxide in nitrogen at nominal concentrations of 1% and 0.1% carbon monoxide. The concentration values determined analytically by NIST agreed with those determined by NMI to 0.08% and 0.10% relative, respectively. The next two mixtures contained propane at nominal concentrations of 0.3% and 0.05%. The agreement between NIST and NMI was 0.16% and 0.01% relative, respectively. In the last set, the agreement for the mixture containing nominal 2.5% carbon dioxide was 0.05% relative while the agreement for the mixture containing nominal 0.5% carbon dioxide was 0.13% relative.

The comparison of all the results show that for the analytes of carbon monoxide, propane and carbon dioxide, there is better than a 0.2% relative agreement between the two laboratories in the concentration range of 0.05 to 2.5%. The overall uncertainty in the NIST analytical procedures was approximately 0.15% relative. This shows that there is no true difference in the quality of the standards of the two laboratories. This is the foundation from which other intercomparisons will be made. Different analytes and lower concentrations will be studied in the future. The NMI is coordinating a round robin intercomparison which involves the analysis of 15 other gas mixtures. Work on the program, which is sponsored by the International Committee on Weights and Measures (CIPM), will be completed in the next year.

Gas Permeation tubes containing SO<sub>2</sub> are also produced by NIST and NMI as standards. The Gas Metrology Group is currently exchanging SO<sub>2</sub> permeation tubes with NMI to study incomparability and international shipping effects on permeation rates. Concurrently, we are studying the effects of domestic shipping on permeation rates. This study is necessary because international shipping involves extremes in temperature and pressure. Also it frequently requires extended transportation time due to holding periods at borders, and multiple transportation methods causing any coolant to be exhausted. This study will continue next year and hopefully will result in shipping methods that will preserve the reservoir of SO<sub>2</sub> and the permeation rates.

## **17. Development of Standardized Protocols for Automated Analytical Systems**

**G.W. Kramer and F.R. Guenther**

In 1990, NIST joined with interested parties from the private sector and other Government agencies to form the Consortium on Automated Analytical Laboratory Systems (CAALS), to foster the development and use of automation in analytical chemistry. From the CAALS viewpoint, fully automated analytical systems can best be constructed by interconnecting instrument modules designed specifically for machine-controlled system use instead of human-operated stand-alone devices, with controllers to form integrated workcells.

CAALS is focusing its efforts on the interfaces between the modules and the controller, for it is at such interfaces that standardized component behaviors become essential to system integration. Successful module-to-controller integration involves electronic interfaces for data and control/status interchange as well as physical interfaces for samples and materials. Since other groups, such as the Analytical Instrument Association, are developing standards for data interchange, CAALS has concentrated on the control/status and physical interfaces. To bridge the chasm created by the use of multiple computing platforms, operating systems, and physical links between instruments and controllers, CAALS has developed its CAALS-I Communication Specification.

The CAALS-I Communication Specification for module-to-controller messaging specifies a communication protocol (rules about who gets to talk and when) and a message syntax (how the messages are formatted). It does not describe message semantics (the content of messages). CAALS-I was created as part of an overall scheme to develop a modular approach to analytical system building, where components can be inserted as needed in a simple plug-and-play fashion without the expense and difficulties experienced in creating today's custom systems. Although the CAALS working group searched, it was not able to find a single, existing communication specification that met its requirements for analytical laboratory systems. CAALS-I was created from existing standards and current practices, expressly minimizing incorporation of new, untested concepts. Currently, CAALS-I supports a variety of links (IEEE-488, RS-232, and DDE) and can be adapted to other connection schemes such as TCP-IP. By providing a client-server approach with guaranteed connectivity and error-free message delivery that is applicable to small, embedded microcontroller applications as well as larger computers, CAALS-I provides a generic communication scheme which cuts across operating system and computing platform barriers. Over the past summer, CAALS conducted an external review of CAALS-I to detect problems with, and increase awareness of, this Communication Specification. The formal document describing the specification is currently being written and is slated for completion in December.

Writing a specification is one aspect of the problem, but getting industry to accept it is yet another. To make using CAALS-I easier, and hopefully more appealing, CAALS is implementing its specification on a variety of computing platforms with several different links to provide actual working examples. These implementations will be made available as addenda (with both documentation and actual code) to the formal specification. At this time, implementations are being developed for modules using three different types of embedded microcontrollers, for both PC-based modules and controllers using Windows and for a Windows NT-based controller. A first generation compliance testing tool for modules, being created to evaluate the robustness of module implementations, will also be available as an addendum to the CAALS-I specification. Finally, a guide to implementing CAALS-I with suggested application programming interfaces for several computing environments and examples of single-tasking, multi-tasking, threaded, etc. implementations is planned for next year.

## 18. Development of An Improved Titrimetric Method for SO<sub>2</sub> in Gas Cylinders

G.D. Mitchell and W.J. Thorn

The Clean Air Act as amended in 1990 established the Acid Rain Program which requires large utilities to expand their sulfur dioxide (SO<sub>2</sub>) monitoring using instruments calibrated with NIST "traceable" gas standards. This requirement has caused an increased demand for NIST SO<sub>2</sub> in nitrogen SRMs; along with interest in the development of lower uncertainties for these SRMs.

NIST assigns SO<sub>2</sub> concentrations using a primary method which involves the oxidation of adsorbed SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub> followed by acid-base titration. This method has proven reliable over the last ten years providing concentrations with measured uncertainties between one and two percent relative; estimated at the 95 percent statistical confidence level.

The key steps in our primary method were critically reviewed and improvements in the methodology were developed. These improvements are:

1. The 0.05 N NaOH usually prepared as needed in 2 liter quantities was purchased commercially in a 40 liter quantity allowing for periodic standardization against NIST acidimetric SRMs. This avoids possible random errors associated with the frequent preparation and standardization of base in small volumes; and provides for a historical record eliminating a possible source of concentration bias.
2. The operation of our Metrohm automatic titrator was optimized to allow a precision of  $\pm 0.2\%$ . The development of a closed NaOH feed system to the titrator has eliminated the need for an ascarite CO<sub>2</sub> scrubber.
3. An improvement in the assignment of normality to the standard base was achieved by performing replicate determinations with standard solutions of potassium hydrogen phthalate (KHP) and hydrochloric acid at appropriate concentrations. The KHP standard solution was prepared gravimetrically, while the hydrochloric acid solution was assigned a concentration value from high-accuracy coulometric measurements. The two methods agreed within  $\pm 0.1$  percent relative to the normality of the NaOH.
4. The precision of the wet-test meter used for measuring the gas volume was improved by increasing the volume of gas sampled from 3 liters to 9 liters; while maintaining the resolution of the wet-test meter at 10 mL. This represents an improvement in relative precision of this volume measurement of from 0.3% to 0.1%.
5. An observed slight dependance of the SO<sub>2</sub> concentration values on the barometric pressure has been empirically quantified to allow correction of all measurements to 751.5 Torr which is the mean for the laboratory. We hope to resolve and eliminate this effect in future work.

These improvements have resulted in lowering the uncertainty of SO<sub>2</sub> primary method uncertainty to less than one percent relative (95% CI) based on measurements from the certification of recent SO<sub>2</sub> in nitrogen SRMs with concentrations between 260 μmol/mol and 3500 μmol/mol.

#### 19. Certification of Natural-Matrix SRMs for Monitoring Organic Contaminants in the Marine Environment

S.A. Wise, B.A. Benner, Jr., M.J. Hays, B.J. Koster, and M.M. Schantz

In 1989 and 1990 two Standard Reference Materials (SRMs) for organic contaminants in marine samples were issued: SRM 1941, Organics in Marine Sediment, and SRM 1974, Organics in Mussel Tissue (*Mytilus edulis*). These two materials were the first of three marine matrix SRMs that were prepared by NIST at the request of the National Oceanic and Atmospheric Administration (NOAA) to support their marine pollution monitoring programs. Both of these SRMs have assigned concentrations for trace level organic contaminants including selected polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and chlorinated pesticides. SRMs 1941 and 1974 have found widespread use in marine monitoring programs, and as a result the original supplies of SRM 1941 and 1974 were depleted in 1993. The reissue of both SRMs 1941 and 1974 is currently in progress. To expand the usefulness of the reissues of SRMs 1941 and SRM 1974, we would (1) collect larger quantities of sediment and tissue to provide sufficient material to extend the availability of these SRMs to 7-8 years since SRMs 1941 and 1974 were depleted in 3-4 years; (2) provide "certified" values for a significantly larger number of organic contaminants than the original SRMs; and (3) reduce the uncertainties associated with the reported contaminant concentrations.

In August 1991 a new sediment material was collected at the same Baltimore harbor location as the material used for SRM 1941. The sediment material was freeze-dried and then sieved to obtain the 150 to 250 μm particle size fraction for use as SRM 1941a. In October 1992 approximately 6000 mussels were collected at the same Boston Harbor location as the mussels used for SRM 1974. Approximately 80 kg of tissue was obtained from the mussels and was cryogenically homogenized to prepare SRM 1974a. The quantities of sediment and mussel tissue represented nearly three times the amount of material collected for the original SRMs.

The analytical measurements for the certification of the marine sediment (SRM 1941a) have been completed. Three approaches have been used for the determination of the PAHs: gas chromatography-mass spectrometry (GC-MS) on a 5% phenyl-substituted methylpolysiloxane stationary phase; GC-MS on a smectic liquid crystalline stationary phase; and reversed-phase liquid chromatography with fluorescence detection. The 5% phenyl-substituted methylpolysiloxane column represents the typical GC stationary phase used for PAH analyses. The liquid crystalline column provides separation of several PAH isomers that are not separated on the 5%-phenyl methylpolysiloxane column. These two GC methods are complemented by

reversed-phase LC procedures with fluorescence detection, including multidimensional LC procedures to quantify several PAHs that are difficult to measure due to low concentrations and/or low selectivity of the fluorescence detection. Based on the agreement of results from these three approaches, certified values were determined for 23 PAHs; noncertified concentrations, which were determined using only one technique, are reported for an additional 20 PAHs. For the PCBs and chlorinated pesticides, GC with electron capture detection (GC-ECD) and GC-MS on two columns with different selectivity were the analytical techniques used to determine certified concentrations for 22 PCB congeners and 6 chlorinated pesticides. Noncertified concentrations are also reported for 18 aliphatic hydrocarbons determined by GC-MS and for 24 inorganic constituents determined by instrumental neutron activation analysis. The number of analytes with certified and noncertified concentrations for SRM 1941a greatly exceeds the analytes measured in SRM 1941 (certified concentrations for only 11 PAHs and noncertified concentrations for 15 PCB congeners, 7 pesticides, and 24 additional PAHs). SRM 1941a currently has the largest number of certified concentrations for PAHs, PCBs, and pesticides for any natural environmental matrix SRM issued by NIST. The uncertainties associated with the certified concentrations ranged from 3 to 14% for all but two of the 23 PAHs and were decreased for 9 of the 11 PAHs certified in the previous material.

The certification measurements for PAHs, PCB congeners, and pesticides in SRM 1974a are currently underway using the same approaches as used for SRM 1941a. The third material requested by NOAA is SRM 1945, Organics in Whale Blubber. The certification measurements for PCB congeners and chlorinated pesticides in SRM 1945 have been completed using GC-MS and GC-ECD as described above for the sediment, resulting in certified concentrations for approximately 25 PCB congeners and 15 chlorinated pesticides.

These three SRMs will assist in validating the accuracy of analytical measurements associated with several marine monitoring programs supported by NOAA and the U.S. Environmental Protection Agency.

## **20. Health and Nutrition Related SRM Activities**

**M.J. Welch, S.S.-C. Tai, P. Ellerbe, R.G. Christensen, J.M. Brown Thomas, N.E. Craft, S.A. Margolis, and K.S. Sharpless**

Disease prevention is far more cost effective than disease treatment. Evidence for the importance of carotenoids and vitamins in prevention of cancer and heart disease continues to grow. This evidence, plus the increased labeling requirements on foods, are driving the food industry to make more and better measurements on nutrients in foods. To address this growing need, NIST is developing a reference material (candidate SRM 2383) for carotenoids and vitamins in food. Because baby foods are formulated, processed, and packaged in such a way that carotenoid and vitamin levels are relatively high and shelf stability is quite long, a composite baby food material was deemed the best choice. A material was prepared and bottled at Gerber Products Company.



The recipe devised at NIST was based upon prior studies. The material was a blend of orange juice concentrate, powdered infant formula, corn, tomato paste, carrots, and many other ingredients. Preliminary measurements using liquid chromatography have found the levels of the carotenes, xanthophylls, retinol, and tocopherols to be satisfactory. Certification measurements will be undertaken in FY94.

Drug abuse continues to be a serious social problem and drain on the U.S. economy. Drug testing programs for current employees and potential new employees are in widespread use, as U.S. industry strives to create drug-free environments to improve productivity and reduce health-care costs. NIST has a long-standing effort in cooperation with the College of American Pathologists and the Armed Forces drug testing program to provide urine-based SRMs with certified concentrations of drugs of abuse. The most recent material, SRM 1511, contains the seven compounds that must be tested for in Federally mandated drug testing programs. Each of these compounds is present at a level that is within  $\pm 10\%$  of the cutoff level specified in the Federal regulations. Certification of each of the analytes in this material involves a combination of two independent analytical methods, one of which involves gas chromatography/mass spectrometry and the other involves liquid chromatography with either UV or mass spectrometric detection. Certification measurements are completed for most of the analytes with the remaining measurements scheduled for early FY94.

Probably the most important SRM for health measurements is SRM 909, human serum. Many clinically important analytes are certified in this material by Definitive Methods developed in this Division and in Division 834. The present lot, SRM 909a, will be out of stock in FY94 and must be replaced. Scientists in Division 835 have been active in providing specifications for analytes, levels, moisture, and homogeneity for the new lot, 909b to be acquired and certified in FY94. This material will consist of two levels (normal and elevated) for most major analytes. This new material should have a lower and more uniform water content, thus improving the stability of glucose, which was a major problem with the 909a material. New measurement technologies, involving electrospray mass spectrometry, are being developed in the Division and may be applied to the determination of albumin and other important serum proteins in this material.

C. **Outputs and Interactions**  
(Organic Analytical Research Division)

1. **Publications**

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- Wise, S.A., "Quality Assurance of Contaminant Measurements in Marine Mammal Tissues," In: Coastal Zone '93 Proc. of Eighth Symposium on Coastal and Ocean Management, 2531-2541 (1993).
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## 2. Talks

- Benner, B., Jr., "Standard Reference Materials for Use in Supercritical Fluid Extraction Method Development," American Chemical Society, Denver, CO, March 31, 1993. Invited
- Benner, B., Jr., "Measurement of Polycyclic Aromatic Hydrocarbons in Extracts of Aerosol Samples Collected in Roanoke, Virginia," International Symposium of Toxic and Related Air Pollutants, Durham, NC, May 4, 1993.
- Brown Thomas, J., "Stability of Vitamins and Carotenoids in Serum," NIST/NCI QA Micronutrient Analysis Workshop, Rockville, MD, November 14, 1992.
- Choquette, S., "Fiber Optic Interferometry for Thermal Immunosensing," Biomedical Engineering Society, University of Utah, Salt Lake City, UT, October 17, 1992. Invited
- Choquette, S., "Planar Waveguide Immunosensors," Georgia Institute of Technology and Photonic Sensors Systems, Atlanta, GA, January 12, 1993. Invited
- Choquette, S., "Planar and Fiber Waveguide Optical Immunosensors," ERDE, Department of Defense, Aberdeen Proving Ground, MD, January 14, 1993. Invited
- Choquette, S., "Optical Fiber and Planar Waveguide Research at NIST," Paracelsian, Inc., Ithaca, NY, March 9, 1993. Invited
- Craft, N., "Correlations Between Measurement Method and Practice vs Data Quality," NIST/NCI QA Micronutrient Analysis Workshop, Rockville, MD, November 14, 1992.
- Craft, N., "Effect of Sample Preparation on Fat-Soluble Vitamin and Carotenoid Concentrations," Federation of American Societies for Experimental Biology (FASEB), New Orleans, LA, March 31, 1993.
- Dorko, W., "NIST Traceable Reference Material Program," Workshop on New NIST Gas Standards Programs, Atlanta, GA, March 9, 1993
- Dorko, W., "Primary Gas Standards: Preparation, Verification, and Uncertainty Determination," Industrial Technology Research Institute, Center for Measurement Standards, Hsinchu, Taiwan, April 15, 1993. Invited
- Dorko, W., "The NIST Gas Standard Reference Material Program," Industrial Technology Research Institute, Center for Measurement Standards, Hsinchu, Taiwan, April 20, 1993. Invited
- Dorko, W., "Gas Standards for Traceable Measurements," Industrial Technology Research Institute, Center for Measurement Standards, Hsinchu, Taiwan, April 22, 1993. Invited

- Dorko, W., "Calibration Mixtures for Gas Sensor Development and Evaluation," Workshop on Gas Sensors; Strategies for Future Technologies, NIST, September 8, 1993.
- Duewer, D., "Implementation and Characterization of a Robotic Protocol for the Extraction of Fat-Soluble Vitamins in Human Serum, International Symposium on Laboratory Automation and Robotics, Boston, MA, October 28, 1992.
- Duewer, D., "Automated Serum Extraction," NIST/NCI QA Micronutrient Analysis Workshop, Rockville, MD, November 14, 1992.
- Duewer, D., "Preliminary Results from the TWGDAM Precision Studies," 2nd International Symposium Forensic Aspects of DNA Analysis, Quantico, VA, April 2, 1993.
- Emery, A., "Supercritical Fluid Extraction in Phospholipids," American Chemical Society, Denver, CO, March 31, 1993.
- Gray, M., "Immunoassay Studies of Cholesterol Related Lipoproteins," Howard University, Washington, DC, February 12, 1993.
- Guenther, F., "Creating MS-Windows Dynamic Link Libraries for a CAALS Standard Laboratory Module," Scientific Computing and Automation Meeting, Crystal City, VA, October 15, 1992.
- Guenther, F., "A Fully Automated System for the Analysis of Diesel Hydrocarbons in Soils," Mid-Atlantic American Chemical Society Meeting, Crystal City, VA, December 9, 1992.
- Guenther, F., "NIST CAALS: Description of the Standard Interface Within an Automated Chemistry Workcell," Pittsburgh Conference, Atlanta, GA, March 9, 1993.
- Locascio-Brown, L., "Assessing Breast Cancer Risk: Measuring Trace Levels of Hormones by FIIA," NIST QA Micronutrient Analysis Workshop, Gaithersburg, MD, November 14, 1992.
- Locascio-Brown, L., "Immunosensing in Flow Injection Analysis Using Liposome Amplification," Winter Conference on Flow Injection Analysis, Marathon, Florida Keys, January 4, 1993.
- Locascio-Brown, L., "Integrated Flow Immunoanalysis Systems and Sensor Research at NIST," ERDEC, Department of Defense, Aberdeen Proving Ground, MD, January 14, 1993. Invited
- Locascio-Brown, L., "Measurement of Estrogens by Flow Injection Immunoassay," Paracelsian, Inc., Ithaca, NY, March 9, 1993. Invited

- May, W., "NIST Research and Measurement Activities in Organic Analytical Chemistry," Morgan State University, Baltimore, MD, February 12, 1993. Invited
- May, W., "Environmental Monitoring and Support: NIST Research and Service Activities", U.S. Environmental Protection Agency, Quality Assurance Research Branch, Las Vegas, NV, March 2, 1993. Invited
- May, W., "NIST Traceable Reference Material Program," Workshop on New NIST Gas Standards Programs, Atlanta, GA, March 9, 1993.
- May, W., "NIST Research and Measurement Activities in Organic Analytical Chemistry," University of Maryland, College Park, MD, April 8, 1993. Invited
- May, W., "New Career Opportunities in Chemistry for the 1990's and Beyond," Howard University Honors Convocation, Department of Chemistry, Washington, DC, April 26, 1993. Invited
- Margolis, S., "Measurement of Ascorbic Acid and Isoascorbic Acid in Serum and Infant Formula Using Electrochemical Detection," Federation of American Societies for Experimental Biology (FASEB), New Orleans, LA, April 1, 1993.
- Mitchell, G., "Calibration Mixtures for Gas Sensor Development and Evaluation," Workshop on Gas Sensors: Strategies for Future Technologies, NIST, Gaithersburg, MD, September 8, 1993.
- Page, S., "Evaluation of Fluid Phase Behavior on Supercritical Fluid Chromatographic Performance," NATO Advanced Study Institute, Antalya, Turkey, July 21, 1993.
- Parris, R., "Gas Chromatographic Determination of Individual Polychlorinated Biphenyls Congeners and Chlorinated Pesticides in Environmental Matrices," Eastern Analytical Symposium, Somerset, NJ, November 19, 1992. Invited
- Parris, R., "Use of QA in Data Interpretation," NOAA Damage Assessment Center QA Workshop, NOAA, Rockville, MD, December 16, 1992.
- Parris, R., "Determination of Planar PCB Congeners in a Cod Liver Oil Reference Material," Pittsburgh Conference, Atlanta, GA, March 10, 1993.
- Parris, R., "Components of a Performance-Based Analytical Quality Assurance Program for an Environmental Monitoring Program-The NIST/NOAA NS&T Organic QA Program, Pittsburgh Conference, Atlanta, GA, March 11, 1993.
- Rhoderick, G., "Methyl Bromide and Methyl Chloride Gas Standards," NOAA/CMDL Annual Meeting, Boulder, CO, March 3, 1993.



- Rhoderick, G., "Radiocarbon Measurements of Urban Tropospheric Carbon Monoxide: Use of a Factorial Design Sampling Strategy," Spring AGU Meeting in Baltimore, MD, May 25, 1993.
- Sander, L., "Shape Discrimination of Polycyclic Aromatic Hydrocarbon Isomers in Liquid Chromatography," Pittsburgh Conference, Atlanta, GA, March 11, 1993. Invited
- Sander, L., "Development of Tailored Stationary Phases for the Separation of Carotenoid Isomers," 17th International Symposium on Column Liquid Chromatography, Hamburg, Germany, May 10, 1993.
- Sander, L., "Shape Selectivity in Liquid Chromatography," Department of Analytical and Environmental Chemistry, Universität Ulm, Ulm, Germany, May 7, 1993. Invited
- Schantz, M., "Comparison of NIST Results with Certified Values of Selected Pesticides and PCBs in BCR Reference Materials," National Status and Trends Program 1992 Quality Assurance Workshop, Gaithersburg, MD, December 9, 1992.
- Schantz, M., "Standard Reference Materials (SRMs) for Polychlorinated Biphenyls (PCBs) and Their Applicability to Toxaphene Measurements," Burlington, Ontario, Canada, February 5, 1993.
- Schantz, M., "Development of a Frozen Whale Blubber Reference Material for the Measurement of Polychlorinated Biphenyls (PCBs) and Chlorinated Pesticides," Pittsburgh Conference, Atlanta, GA, March 10, 1993.
- Sharpless, K., "Factors Affecting Carotenoid Analysis," NIST/NCI QA Micronutrient Analysis Workshop, Rockville, MD, November 14, 1992.
- Sharpless, K., "New Analytes and/or Methods of Analysis," NIST/NCI QA Micronutrient Analysis Workshop, Rockville, MD, November 14, 1992.
- Thorn, W., "NIST Research Gas Mixtures Program", Workshop on New NIST Gas Standards Programs, Atlanta, GA, March 9, 1993.
- Welch, M., "The Analysis of Hair for Drugs of Abuse Using GC/MS," Greater Washington Area Mass Spectrometry Group, Rockville, MD, October 19, 1992. Invited
- Welch, M., "The Analysis of Human Hair for Drugs of Abuse," Department of Chemistry, George Washington University, Washington, DC, December 4, 1992. Invited
- Welch, M., "The Analysis of Hair for Drugs of Abuse Using GC/MS," Washington Chromatography Group, Rockville, MD, September 16, 1993. Invited

- Wise, S., "Shape Selectivity for Polycyclic Aromatic Hydrocarbons in Liquid Chromatography," Eastern Analytical Symposium, Somerset, NJ, November 17, 1993. Invited
- Wise, S., "Quality Assurance for Chemical Analysis of Marine Mammal Tissues," EPA/NOAA Dolphin Mortality Conference, Pensacola, FL, December 2, 1992. Invited
- Wise, S., "Measurement of Organic Contaminants in Environmental Samples," Department of Chemical Engineering Seminar, University of Alabama, Tuscaloosa, AL, February 11, 1993. Invited
- Wise, S., "Status of the NOAA/NIST Marine Mammal Quality Assurance Program," NOAA Marine Mammal Team of Experts Meeting, Silver Spring, MD, March 3, 1993. Invited
- Wise, S., "Retention Mechanisms Applied to the Analyses of Complex Mixtures in High Performance Liquid Chromatography," Northeast Regional Chromatography Discussion Group, Henrietta, NY, May 4, 1993.
- Wise, S., "Preparation and Certification of SRMs for Organic Contaminants in Environmental Samples," 76th Canadian Society for Chemistry Conference, Sherbrooke, Quebec, Canada, May 25, 1993. Invited
- Wise, S., "Specimen Banking and the Development of Reference Materials," 76th Canadian Society for Chemistry Conference, Sherbrooke, Quebec, Canada, May 25, 1993. Invited
- Wise, S., "Quality Assurance of Contaminant Measurements in Marine Mammal Tissue," 8th Symposium on Coastal and Ocean Management, New Orleans, LA, July 22, 1993. Invited
- Wise, S., "Recent Activities in the Certification of SRMs for PAHs in Environmental Samples," 14th International Symposium on Polycyclic Aromatic Compounds, Lake of the Ozarks, MO, September 10, 1993.

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

Clinical Laboratory Work, M. Welch  
College of American Pathologists (CRADA)

Organic Solvent Extraction of Environmental Pollutants from Contaminated Matrices Using Microwave Heating Technology, S. Wise  
CEM Corporation (CRADA)

Preparation of a Quality Assurance Standard, R. Christensen  
Union Carbide Corporation (CRADA)

Flow Injection Immunoassay for Measurement of Hormone Concentration in Serum, L. Locascio-Brown and S. Choquette  
Paracelsian (CRADA)

Bio/Chemical Reagent Immobilization on Integrated Optic Hartman Interferometers for Immunosensing, S. Choquette and L. Locascio-Brown  
Photonic Sensors Systems (CRADA)

#### 4. Patent Awards and Applications

None

#### 5. SRM Activities

SRM 909a Human Serum  
SRM 968a Fat-Soluble Vitamin in Human Serum  
SRM 1507b Marijuana Metabolite in Freeze-Dried Urine  
SRM 1508a Cocaine Metabolite in Freeze-Dried Urine  
SRM 1511 Multi-Drugs of Abuse in Freeze-Dried Urine  
SRM 1647c PAH in Acetonitrile  
SRM 1649 Urban Dust/Organics  
SRM 1658a 1.2 ppm Methane in Air  
SRM 1661a 475 ppm SO<sub>2</sub> in Nitrogen  
SRM 1662a 975 ppm SO<sub>2</sub> in Nitrogen  
SRM 1668b 100 ppm Propane in Air  
SRM 1671a 345 ppm CO<sub>2</sub> in Air  
SRM 1672a 355 ppm CO<sub>2</sub> in Air  
SRM 1674b 7% CO<sub>2</sub> in Nitrogen  
SRM 1675b 14% CO<sub>2</sub> in Nitrogen  
SRM 1676a 362 ppm CO<sub>2</sub> in Air  
SRM 1677c 9.6 ppm CO in Nitrogen  
SRM 1683b 50 ppm NO in Nitrogen  
SRM 1684b 100 ppm NO in Nitrogen  
SRM 1693a 50 ppm SO<sub>2</sub> in Nitrogen  
SRM 1694a 100 ppm SO<sub>2</sub> in Nitrogen  
SRM 1800 5 ppb NMOC  
SRM 1804 5 ppb VOCs in Nitrogen  
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 2381 Morphine and Codeine in Freeze-Dried Urine

SRM 2382 Morphine Gluronide in Freeze-Dried Urine  
SRM 2383 Carotenoids and Fat-Soluble Vitamins in Food  
SRM 2389 Amino Acid Mixture  
SRM 2627a 5 ppm NO in Nitrogen  
SRM 2628a 10 ppm NO in Nitrogen  
SRM 2642a 7.8% CO in Nitrogen  
SRM 2658a 9.7% Oxygen in Air  
SRM 2659a 21% Oxygen in Air  
SRM 2660 100 ppm NO<sub>x</sub> in Air  
SRM 2730 5 ppm H<sub>2</sub>S in Nitrogen  
SRM 2731 20 ppm H<sub>2</sub>S in Nitrogen  
RM 8509 Moisture in Methanol (100 µg/g)  
RM 8510 Moisture in Methanol (400 µg/g)

**6. SRD Activities**

None

**7. Calibrations**

Airco Specialty Gases  
Air Products  
Florida Dept. of Environmental Regulations  
Liquid Air, Alphagaz  
Liquid Carbonic  
Scott Marin, Inc.  
Scott Specialty Gases  
State of New Mexico  
State of Wisconsin - Department of Natural Resources  
U.S. EPA

**8. Committee Assignments**

**L.E. Locascio-Brown**

CSTL Strategic Planning Committee on Biotechnology

**R.G. Christensen**

NIST Museum Committee  
Washington Editorial Review Board

**W.D. Dorko**

ASTM on Analysis of Ambient Atmosphere  
Steering Committee for Ambient Sulfur Gas Measurement Intercomparison Program,  
NSF Chemical Society of Washington, Meeting Arrangements Committee

**W.E. May**

American Chemical Society Council-Committee on Minority Affairs  
Department of Commerce Diversity Council  
EPA Toxic Substances Control Act, Interagency Testing Committee (DoC Representative)  
Federal Interagency Coordinating Committee for National Human Exposure Assessment  
Survey  
Ford Foundation Predoctoral Fellowship Evaluation Panel  
President, International Society on Polycyclic Aromatic Compounds  
Interagency Committee on Human Nutrition Research  
Interdepartment Minority Health/Science Careers Coordinating Committee (DoC  
Representative)  
National Organization for the Professional Advancement of Black Chemists and Chemical  
Engineers (NOBCCHE)  
NIST African American Affirmative Employment Committee (Chairman)

**W.A. MacCrehan**

CSTL Colloquium Committee  
CSTL Strategic Planning Committee on Chemical Process Technology

**R.M. Parris**

Washington Chromatography Discussion Group (Secretary)

**L.C. Sander**

NIST Research Advisory Committee

**M.M. Schantz**

NIST Child Care Association (Treasurer)  
Washington Chromatography Discussion Group (Program Chairman)

**L.T. Sniegowski**

NIST Child Care Center (Bookkeeper)

**J. Brown Thomas**

SCW Education Committee (Chairman)

**S.A. Wise**

CSTL Strategic Planning Committee on the Environment  
American Chemical Society, Division of Analytical Chemistry, Publicity Committee,  
(Chairman)

**M.J. Welch**

Advisor of Standards Committee of the College of American Pathologists  
CSTL Strategic Planning Committee on Health/Clinical Chemistry  
NCCLS Sub-Committee on Urine Drug Testing  
NCCLS Sub-Committee on Cholesterol in Serum Reference Materials

**E. White V**

EPA Toxic Substances Control Act Interagency Testing Committee (DoC Alternate)

**9. Editorships**

**W.E. May**

Journal of Polycyclic Aromatic Compounds (Editorial Board)

**S.A. Wise**

Fresenius' Journal of Analytical Chemistry (Editorial Advisory Board)  
Journal of Microcolumn Separations (Editorial Advisory Board)

**10. Seminars**

**November 13, 1992**

Dr. Yinfa Ma, Division of Science, Northeast Missouri State University, Kirksville, MO,  
"A Fast Minimicroassay of Serum Retinol (Vitamin A) by High Performance Capillary  
Zone Electrophoresis (HPCZE) with Laser-Excited Fluorescence Detection." (Division  
Sponsor: N.E. Craft)

**January 27, 1993**

Ms. Maureen A. Breitenberg, NIST, Standards Code and Information Program,  
Gaithersburg, MD, "ISO 9000." (Division Sponsor: W.E. May)

**February 8, 1993**

Mr. Donald Dahlberg, Department of Chemistry, Lebanon Valley College, Annville, PA,  
"Multivariate Collaboration Methods: PCR & PLS - What It Can and Cannot Do."  
(Division Sponsor: W.A. MacCrehan)

**February 17, 1993**

Dr. Brian Belanger, NIST, Advanced Technology Program, Gaithersburg, MD, "Status  
Report on the Advanced Technology Program." (Division Sponsor: W. E. May)

**April 29, 1993**

Professor Peter Uden, Department of Chemistry, University of Massachusetts, Amherst,  
MA, "Exploring the Periodic Table with Combined Chromatography-Atomic Emission  
Detection." (Division Sponsor: S.A. Wise)

**May 11, 1993**

Dr. Constance Ann O'Neil, Department of Food Science, North Carolina State University, Raleigh, NC, "Photoisomerization of  $\beta$ -Carotene with Chlorophyll Derivatives as Sensitizers." (Division Sponsor: S.A. Wise)

**May 12, 1993**

Dr. Harold Schmitz, Department of Food Science, North Carolina State University, Raleigh, NC, "Advances in Analytical Methodology for Qualitative Analyses of Carotenoids Present in Biological Tissues." (Division Sponsor: S.A. Wise)

**June 16, 1993**

Dr. Alvin Moore, Jr., Department of Chemistry, University of North Carolina, Chapel Hill, NC, "Two-Dimensional RPLC-Fast-CZE-Analysis." (Division Sponsor: S.A. Wise)

**June 23, 1993**

Ms. Julie Seavey, Battelle Ocean Sciences, Duxbury, MA, "Collection and Analysis of Marine Environmental Samples." (Division Sponsor: S.A. Wise)

**July 15, 1993**

Dr. Steven Rhodes, FCR/NCI, Frederick, MD, "Baseline Studies of Indoor Air Quality." (Division Sponsor: M. J. Welch)

**July 22, 1993**

Dr. Mariam Monshipouri, Naval Research Laboratory, Washington, DC, "Liposome Encapsulated Alginate: Controlled Hydrogel Particle Formation and Release." (Division Sponsor: S.J. Choquette)

**July 27, 1993**

Dr. Victoria McGuffin, Department of Chemistry, Michigan State University, East Lansing, MI, "Thermodynamic Studies of Solute Retention in Reversed-Phase Liquid Chromatography." (Division Sponsor: S.A. Wise)

**August 5, 1993**

Mr. Curtis Phinney, Water Resources Division, U.S. Geological Survey, Reston, VA, "A Comparison of Two Analytical Techniques for Identifying and Measuring the Concentration of Volatile Organic Compounds in Ground Water" (Division Sponsor: M. J. Welch)

**August 18, 1993**

Dr. Harry S. Hertz, Office of Quality Programs, NIST, Gaithersburg, MD "Overview of the Malcom Baldrige Quality Awards Program." (Division Sponsor: W. E. May)

**August 25, 1993**

Professor Jan Andersson, Department of Analytical Chemistry, Institute of Inorganic Chemistry, University of Münster, Münster, Germany, "The Use of the Atomic Emission Detector (AED) for the Quantitation of Polycyclic Aromatic Sulfur Heterocycles in SRMs." (Division Sponsor: S.A. Wise)

**September 2, 1993**

Ms. Isabel Caputa, Department of Chemistry, University of Cincinnati, Cincinnati, OH, "Evaluation of Environment Monitoring Assessment Program (EMAP) Samples for Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCBs)." (Division Sponsor: S.A. Wise)

**September 10, 1993**

Mr. Barry Wise, Molecular Science Research Center, Battelle Pacific Northwest Laboratory, Richland, WA, "Second Order Instruments: The Coming Revolution in Sensors." (Division Sponsor: D.L. Duewer)

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

**November 13, 1992**

Fat-Soluble Vitamin and Carotenoid Analysis Tutorial, NIST, Gaithersburg, MD. (W.E. May)

**November 14, 1992**

NIST/NCI QA Micronutrient Analysis Workshop, Rockville, MD. (W.E. May)

**December 8, 1992**

NIST/NOAA NS&T/EPA EMAP Quality Assurance Workshop, NIST, Gaithersburg, MD. (S. Wise)

**March 9, 1993**

New NIST Gas Standards Programs and Services Workshop, Atlanta, GA. (W.E. May and W. Dorke)

**May 21, 1993**

NIST Workshop on the Analysis of Hair for Drugs of Abuse, NIST, Gaithersburg, MD. (M. Welch)

**September 24, 1993**

Fat-Soluble Vitamin and Carotenoid Analysis Tutorial, NIST, Gaithersburg, MD. (J. Brown Thomas and K. Sharpless)



## 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 flow rate (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, 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 and engineering data.

Accurate measurements for process and quality control require validation of measurement methods and calibration of instruments using techniques traceable to national standards. Therefore, **calibration services** represent a very important part of our activities, with over 1000 standard tests and calibrations performed this year. These involved airspeed, fluid flowrate, humidity, liquid density, temperature, 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 we completed a multiyear laboratory development project directed towards full **implementation of the new International Temperature Scale (ITS-90)**. Two new facilities have been developed: one to implement ITS-90 below 84 K and the other to provide efficient calibrations in the range 0.65 to 85 K.

In the area of **humidity standards** we have been working toward the goal of extending the measurement range down to 20 ppbv; currently we calibrate to 3 ppmv (-70 °C frostpoint temperature). This extension is required to enable the U.S. semiconductor manufacturing industry to accurately monitor water vapor, considered the most important contaminant, in process gases. This year we have re-examined our approach to the low-frost point humidity generator taking into account the goals of eliminating the use of potentially harmful liquid baths (e.g., CFCs) and costly, inefficient liquid cryogenes, and providing all-metal sealing technology to assure accuracy in the ppb range of moisture measurement. An extensive engineering study has resulted in a new design which holds great promise to significantly improve all our humidity generation instrumentation. A prototype saturator, utilizing a combination of heat-pump and thermoelectric cooling technology, has been constructed. Tests in the coming year will be

directed toward verification of the initial design goal of 0.05 °C temperature uniformity in the saturator, and are expected to demonstrate as much as an order of magnitude better uniformity in temperature. Performance at this level should be sufficient for accurate humidity generation into the upper range (to +40 °C dewpoint) of NIST calibrations.

The demands of technology are driving similar efforts to improve accuracy and efficiency in almost every area in which we provide calibration services; this is particularly true in the area of **gas and fluid flowrate standards**. For example, semiconductor manufacturing requires accurately known flows of process gases in fabrication units. In a collaborative effort with SEMATECH, an initial accuracy goal of 0.125% has been established for the calibration of mass flow controllers. This will require at least a factor of 2 improvement in current NIST standards, and needs for further improvements in accuracy can be expected to arise. In response to these trends, we initiated efforts to improve the accuracy of our low-range gas flow standards (piston provers) and have, for the first time, used computational fluid dynamics (CFD) to provide quantitative information on the effects of transient and non-ideal flow conditions on the performance of these instruments. This approach will provide the basis for design of more accurate standards and the ability to assess the importance of (and correct for) unavoidable flow induced effects. As metering applications expand and accuracy demands increase, the role of CFD in providing a basis for extending and improving the performance of metering technologies also will increase. Initial areas of interest for our flow program are expected to be orifice meters (of wide use for custody transfer, for example, in the gas industry) and thermal mass-flow controllers (important in the semiconductor industry).

**International intercomparisons** are an important part of maintaining the U.S. national standards of measurement and this year we had efforts joint with PTB (Germany), VSL (the Netherlands), CMS/ITRI (Taiwan), and NPL (the United Kingdom) in the area of temperature and with NRLM (Japan) in air speed. In another international collaboration, we have worked closely with guest scientists from CENAM (Mexico) in both the temperature and flow standards areas with the goal of establishing standards traceable to NIST in this new national metrology laboratory. We also conduct interlaboratory **comparisons within the U.S.** For example a gas flow round robin testing program was completed this year with SEMATECH member laboratories. This program not only revealed discrepancies in mass flowrate calibrations, up to  $\pm 8\%$  among laboratories whose accuracy quotes ranged between 0.1% and 0.5%, but also served to identify means of reducing these measurement errors and produced a new NIST calibration service to assure continued high quality measurements in this area.

A very significant portion of the Division's research effort is focussed on **sensors and transducers**. A major milestone was achieved in this area with the completion of the determination of new reference functions, based on the new International Temperature Scale of 1990 (ITS-90), for all Instrument Society of America (ISA) letter-designated **thermocouples**, the most widely used industrial temperature transducers. This outstanding effort has resulted in the publication of NIST Monograph 175, "Temperature-Electromotive Force Reference Functions and Tables for the Letter-designated Thermocouple Types Based on the ITS-90,"

which will be the defining document for industrial and calibration laboratory thermocouple thermometry throughout the world. We have continued a collaboration with the Semiconductor Electronics Division of the Electronics and Electrical Engineering Laboratory in the area of **sensor arrays**. In this effort, SiO<sub>2</sub> 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 element above a pit etched in the silicon chip and add chemical sensing capability with an overlayer of, for example, SnO<sub>2</sub>. 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. A sensor test facility for assessing the performance of these sensor arrays also was commissioned this year. The opportunities afforded by the combination of this array technology with ultrathin film sensor materials is expected to be a central focus of our gas sensing effort in coming years. As a part of our planning in this area, a very successful **workshop** on "Gas Sensors: Strategies for Future Technologies" was held in September 1993.

In addition, this year saw an expansion of our research into the use of **self-assembled monolayers (SAMs)** for sensor applications. For example, a method to photolithographically pattern SAM films with micrometer spatial resolution has been developed. This provides excellent spatial control of differing terminal functionalities of SAMs having potential for the development of patterned **multi-element, SAM-based biosensors**. We have also examined the lattice structure of SAMs using a recently developed high resolution scanning tunneling microscope (STM). STM images of unprecedented quality have been obtained and previously unknown structures and spontaneous patterning have been observed.

In addition to these areas of process measurement and control, the Division has a growing effort in **process technology** with a primary focus on **high technology materials** and, to a lesser extent, **environmental concerns**. The Division's work in these areas saw a significant expansion in recent years into the area of computational chemistry. Our work includes ***ab initio* molecular orbital and reaction rate theory** combined to yield kinetic rates for ceramic particle nucleation. Such data are necessary for models that are being applied to the design of CVD and nanoparticle synthesis reactors. The computational results differ substantially from what would be predicted using gas kinetic rate constants and explain the experimentally observed behavior of partial oxidation of nanoparticles during their formation from the vapor. Further these results yield a systematic approach to predicting particle formation under CVD conditions. Other crucial steps in particle and surface formation involve clusters in a size regime which is extremely difficult to access experimentally. This has led to a very successful effort in **molecular dynamics** as a tool for understanding and predicting particle formation. This year's accomplishments include algorithm refinement that has allowed for the simulation of clusters of silicon in excess of 1000 atoms and the computational preparation of atomic surfaces of silicon in order to investigate the effects of particle-surface interactions.

Our computational efforts in the process technology area are not limited to molecular level computations. Typically, **computer based process simulations**, including the fluid mechanics of mass and energy flow, 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 year saw the modeling effort in this work move to the development of a control volume model to provide a dynamic description of and real-time control information for 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. Highly specialized experimental systems often are required in such research, and the Division has constructed a number of facilities for the study of high technology materials processing. Recent examples include, a **high temperature materials synthesis reactor**, which focusses on cluster and nanoparticle kinetics, and the **Gaseous Electronics Conference Reference Discharge Cell** which will serve as an experimental platform for understanding the chemistry of plasma enhanced etching.

This year saw an expansion of our efforts to provide process simulations, models, and data, based on both experimental and computational efforts, in the area of **pollution avoidance and waste destruction**. Three groups in the Division participated in a collaborative program with the Building and Fire Research Laboratory, under Air Force sponsorship, to develop criteria for ranking potential replacements for environmentally harmful halon fire suppression agents. This work involved experimental dispersion studies in the Fluid Flow Group, the construction of a turbulent diffusion burner used to measure minimum concentrations of agents required for flame extinguishment in the High Temperature Processes Group, and a very successful effort centered in the Reacting Flows Group, in collaboration with the Chemical Kinetics and Thermodynamics Division, to develop a detailed chemical kinetic mechanism and thermochemical database for fluorocarbon chemistry. This new mechanism currently has over 600 reactions that are being refined to produce a final product that should have application not only to the fire suppression problem but also to low pressure plasma etching.

The Division initiated a **reactor engineering effort** this year with a special emphasis on **environmental concerns and waste treatment**. The interest is to broaden the spectrum of our chemical engineering research to include process simulation and validation applied to prototypical chemical reactors so as to better support the industrial applications of advanced chemical process technologies and to focus our more traditional data and measurements activities. Work in this area has had an initial focus on demilitarization with technical oversight and program management being provided to an Air Force program at Tyndall AFB and an advisory interaction with the Joint Ordnance Commanders Group. We are formulating a role for the Division in the area of waste avoidance and treatment and have conducted two **workshops**: the "Waste Processing and Minimization Workshop" (held in April 1993) evaluated the programs and plans by Federal Government agencies, with Government and National Laboratory personnel as the participants; and the "Workshop on Identification of Critical

Measurement Needs for Waste Minimization from Industrial Processes" (held in September 1993) collected measurement needs as perceived by industrial participants.

As a result of a CSTL reorganization this past year, the Division expanded its program in heat and mass transfer in industrial systems and added expertise in cryogenic systems and refrigeration. The latter effort is a highly successful research program in the development and application of orifice pulse tube refrigerators (OPTR). As part of a 4-year CRADA with Tektronix, the Fluid Systems Group and collaborators at Los Alamos are developing a 400 Hz thermoacoustically driven OPTR to provide 10 K cooling of superconducting electronics. If this innovative development effort is successful, this technology could provide a highly reliable refrigeration system, with no moving parts, for a wide range of low temperature electronic equipment. Other examples of the Division's work in heat and mass transfer include the previously mentioned design of a new approach to humidity generation equipment, validation and design optimization for a new liquid H<sub>2</sub> neutron moderator for the NIST Cold Neutron Research Facility, a joint project with NASA Lewis on design of a thermal vent system for spacecraft fuel storage vessels, and development of a computational fluid dynamics code for variable property supercritical water flows through pipes and heat exchangers. Our efforts in these areas have an important experimental validation component in the research plan.

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 the areas of high technology materials processing, on-line measurements related to supercritical water oxidation and metallorganic chemical vapor deposition, cryogenic refrigeration, accelerated life testing of materials, acoustically driven spray nozzles, and advanced thermally driven waste destruction technology.

During the past year, the outstanding accomplishments of our technical staff have been recognized with a number of awards. Dr. George E. Mattingly was selected as the Department of Commerce Engineer of the Year and was among the 10-finalists for the Federal Engineer of the Year Award. Dr. Michael R. Zachariah received the DoC Bronze Medal for his pioneering chemical engineering research in the production of high technology materials via multiphase chemical reactions. Dr. Weston L. Tew received the NIST Measurement Services Award to recognize his efforts to improve low temperature calibrations. Mr. Pedro I. Espina and Dr. George E. Mattingly were members of a team, from three NIST laboratories, awarded the William P. Slichter Award for their outstanding collaborative research in support of the NIST/industry consortium on metal atomization (SIGMA). Dr. Ray Radebaugh was presented with the 15-Year Appreciation Award of the International Cryocooler Conference for his excellent contributions and outstanding dedication in promoting cryocooler technology.

In FY93 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 Performed by the Process Measurements Division**

**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 temperature, humidity, fluid flow rate, air speed, liquid density and volume measurements. These are listed in the following:

<u>Service</u>	<u>Number of items calibrated</u>	
Fluid Flowrate	36	(28 for industry)
Cryogenic Fluid Flowrate	5	(4 for industry)
Volumetric Containers	84	(83 for industry)
Airspeed devices	61	(59 for industry)
Reference Standard Hydrometers	64	(62 for industry)
Humidity	40	(38 for industry)
Standard Resistance Thermometers	91	(61 for industry)
Thermocouples	151	(146 for industry)
Laboratory Thermometers	312	(296 for industry)
Potentiometers	2	(2 for industry)
Fixed-point cells	7	(7 for industry)

These calibrations generally establish a traceability link between the national standards maintained at NIST and the standards of the requesting laboratories. In this way, a basis is provided for the assurance of measurements produced in the requester's laboratories. We also establish measurement accuracy via formal Measurement Assurance Programs and round robin tests with individual and multiple-laboratory participants.

Our capabilities, experimental techniques and facilities are constantly upgraded to meet demands for improvements in measurement services. Activities in the thermometry area include upgrading the Thermocouple and Liquid-in-Glass Calibration Laboratories and constructing a new facility to replace an extremely antiquated low-temperature calibration system, which was inefficient and very expensive to operate. In the Thermocouple Calibration Laboratories, obsolete equipment is being upgraded, new facilities for calibration of Au/Pt thermocouples were installed, and the efforts to increase laboratory automation were continued. Computer programs used in calibrations of types B, R and S thermocouples were revised to incorporate the new International Temperature Scale of 1990 (ITS-90) reference functions, and to incorporate new and improved methods of data analysis.

In the Liquid-in-Glass Laboratory, automation of many of the measurements is progressing. Because of the many improvements in the instrumentation in this laboratory, we have initiated a new investigation of the uncertainties of calibrations of liquid-in-glass thermometers. Several different types of thermometers that are calibrated in the new high-uniformity, constant-temperature baths put into calibration service over the past few years are included in the study. Also, data were obtained to evaluate the uncertainty of ice baths. New documentation on calibration uncertainties will be issued in the coming year.

The new low-temperature facility, in which calibrations of thermometers between 0.65 K and 84 K will be performed, is nearing completion. The construction, assembly and initial testing of the  $^3\text{He}$  refrigerator and a large part of the ancillary equipment for this facility have been completed. Also, interfacing of equipment for automated measurement has been completed and a technique for testing the vacuum integrity of low-temperature thermometers has been developed. A preliminary evaluation of the facility has been completed and a trial run of comparison calibrations of standard platinum resistance thermometers (SPRTs) and rhodium iron resistance thermometers (RIRTs) is currently underway. Designs of transportable fixed-point cells that will be used for realizing the ITS-90 in the region from 84 K to 13.8 K in this apparatus and for international intercomparisons were completed this year and the cells will be constructed in FY94. Calibrations also will commence in the coming year.

We have improved our air flow calibration services by expanding the previous flow rate range to a 85 cubic meters per minute maximum. This has been achieved through the installation of a new compressor and a new set of valves for the pressure, volume, temperature, and time (P,V,T,t) facility. The characterization of the performance of this facility has been started and this effort shall be central in the Fluid Flow Group's FY94 activities. These efforts are expected to produce uncertainty quotes for the NIST air flowrate calibration facilities of  $\pm 0.2\%$  for the full flowrate range from 5 standard cubic centimeters per minute (sccm) to 85 cubic meters per minute. Flow measurement needs, for example in semiconductor manufacturing, require improvements in our current measurement uncertainties by at least a factor of two. To this end, we initiated an effort this past year to develop a computational fluid dynamics (CFD) based model for the performance of our fluid flow facilities, starting with the piston-prover facilities used for the low-range standards. This effort is expected to improve our confidence in the performance of these standards and to indicate approaches for better instrument design and operating procedures in order to reduce errors.

We have also initiated a new flow calibration service for nitrogen-gas flows at nominally 300 and 800 sccm. These calibrations are done on-site in the customer's laboratories. This approach, based on the success of a recently completed SEMATECH round-robin testing program completed this past year (see report number 4, below), has the advantage that it not only checks the accuracy of the customer's calibration facility, but also allows identification and rapid correction of sources of error.



Efforts to improve humidity measurements and standards have centered on the construction of a new gravimetric hygrometer that serves as the primary method for measurement, and the development of a new design for low-frost-point humidity generation. The objectives for the new design are: (1) achieve moisture concentration values from 10 ppb<sub>v</sub> to 100 ppm<sub>v</sub>, (2) eliminate the liquid CFC thermostating baths and cryogenic cooling currently in use, while maintaining necessary thermal stability (constant saturator temperature within 0.05°C), and (3) take advantage of ultra-pure gas-handling technology. A design which meets all these criteria was achieved and component fabrication/procurement was initiated this past year. The new low-frost-point generator will be commissioned in the coming year. The design study, done jointly with the Fluid Systems Group, included thermal modeling of the proposed saturator structure to investigate temperature gradients in various geometrical designs. The final results indicated that temperature gradients are sufficiently small in these all-copper structures that it may be possible to utilize them for higher temperature operation. A study aimed at a replacement of the 2-pressure generator will be undertaken in FY94. The current system, the mainstay for humidity calibrations, is quite inefficient and costly and a viable approach to replacement has been a concern in recent years. The gravimetric hygrometer is very near completion and is expected to be commissioned in FY94. It will be used to qualify the new low-frost-point generator.

## 2. Special Flow Measurements Projects

**G.E. Mattingly, G.P. Baumgarten, W.G. Cleveland, J.M. Allingham,  
J.D. Siegwarth, and A. Loza-Guerrero (CENAM, Mexico)**

The Fluid Flow Group has progressed significantly in its USN Calibration Coordination Group (CCG) sponsored effort to assess the flowrate measurement accuracy of the Navy's new Flow Calibration Test Stand (FCTS). The Navy's principal interest is the calibration of turbine meters used for improved engine performance testing. The unit is equipped with three differently sized volumetric systems with the goal of achieving a uniform accuracy of  $\pm 0.025\%$ . A significant effort was required this year to achieve reliable operation of the hardware and to improve the design and operation of the software. The largest unit has required extensive adjustments and repairs by the manufacturer and is only now ready for assessment. Preliminary test results indicate that the middle and small units have imprecisions at levels of  $\pm 0.03\%$  and  $\pm 0.05\%$ , respectively. Incomplete knowledge of the viscosity of the prototype hydrocarbon fuel employed in the unit is suspected to be a major source of this imprecision. Additionally, all three units will require their bias errors to be evaluated, by cross-comparison to NIST's mass flow rate based systems, before the accuracy of the FCTS can be quantified. These efforts are expected to be continued under Navy sponsorship in the future.

We have also conducted the first of three interlaboratory cross-check tests to assess the water flow measurement accuracy of the Naval Ship Systems Engineering Station (NAVSSSES) in Philadelphia. As a part of this work, we designed and constructed a flow artifact, a dual turbine

meter assembly, and a measurement procedure to enable these flow facility intercomparisons. Results indicated that for the conditions tested, 38-144 liters/min (10-30 gal/min) in a 3.81 cm (1.5 in) pipe, NAVSSES results were within  $\pm 0.3\%$  of NIST values. These results confirmed the NAVSSES accuracy quote of  $\pm 0.5\%$  for the calibration facilities involved. Two remaining testing phases are scheduled for FY 94. The transfer standards used for these tests are designed for use in other testing laboratories, both national and international.

Research has been underway in the Fluid Systems Group for several years to produce flow instrumentation that could improve the safe operation and improve efficiency of the Space Shuttle Main Engine (SSME). The liquid hydrogen fuel and the liquid oxygen (LOX) flows in the ducts of the SSME divide into several routes between the supply pumps and the combustion chamber. The efficiency of the engine depends in part on this division. Currently, flow control is limited to using preset flow resistances in the ducts because of the difficulty of placing satisfactory meters in these short ducts containing many bends. Additionally, flow velocities are up to five times higher than the maximum velocities to which conventional flowmeters can be subjected. We continue to develop and test vortex shedding flowmeters, of various sizes, capable of measuring flows under these extreme conditions.

This year a 5.08 cm (bore) meter of NIST design was manufactured of a material suitable for testing in the NASA Technology Test Bed, a prerequisite to installation on the SSME. This meter also was successfully tested at liquid nitrogen temperature and hydrostatically tested (using water) at 69 MPa to demonstrate that it would withstand the pressure and temperature environment of the SSME ducts. An anomalous result has been observed in the performance of the meter in that it performed better when installed in the complex geometry typical of an SSME duct than when it was installed in a straight test section. Tests this coming year will be made in ducts that very closely resemble the actual engine configuration in order to assure the meter's accuracy for the proposed engine applications.

### **3. Flowmeter Standards for Custody Transfer**

**G.E. Mattingly, T.T. Yeh, J.M. Allingham, J.L. Scott, and M.A. Lewis**

This research program has the objective of characterizing and improving flow measurement accuracy in "non-ideal" installation conditions for applications involving, for example, natural gas and commercial steam transfer. There are two major parts to this effort; the first uses laser Doppler velocimetry (LDV) in a water flow facility to characterize pipeflows downstream of prevalently used piping configurations. These data along with a small number of meter calibration results obtained in the presence of the configuration can be used to satisfactorily predict meter performance in other untested installation positions. A second part of the effort, centered around support of custody transfer in the gas industry, provides critical engineering test data on high-pressure gas flows under Reynolds number conditions closer to those experienced in industrial metering applications. The data are part of an effort to develop improved standards

of practice and new approaches to more accurate gas metering. In addition, these efforts produce: (1) fundamental, fluid mechanical understanding of these flows; (2) parameterization of the salient anomalous flow features to predict meter performance; (3) the proper technical basis for updating or producing new national and international metering standards; and (4) data for initiating and validating computational fluid dynamics (CFD) models developed to understand more completely these and other non-ideal flows.

The latest phase of the LDV effort has focussed on the 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 selection and design of the header is done in collaboration with the NIST Fluid Meter Installation Effects Consortium and with gas industry participation. The results obtained show that very high levels of pipeflow swirl and severe skewness of the axial velocity profiles can be produced for routine operating conditions. We have shown that these, in turn, significantly perturb the performance characteristics of both a standard turbine meter and a range of orifice meters.

The study of installation effects on orifice meters using high pressure nitrogen gas is the principal part of the Fluid Systems Group contribution to this research. During FY93, the research focus was the 100 mm and 150 mm orifice meters. This complemented the FY92 work with the 50 mm orifice meter. We tested the performance of these orifice meters, both with and without flow conditioning, in various configurations common to the gas industry. We found that the discharge coefficients of the orifice meter generally are affected by subtle changes in the flow field and that these effects are not predictably eliminated when standard flow conditioners are employed. These results and those coming from our previous efforts have produced a renewed interest on the part of the Gas Research Institute (GRI) in the development of improved flow conditioners. Much of this new work currently is centered at the GRI sponsored Southwest Research Institute.

#### **4. Improved Gas Flow Traceability for the U.S. Semiconductor Processing Industries**

**G.E. Mattingly, G.P. Baumgarten, P.I. Espina, J.M. Allingham, and W.G. Cleveland**

The Fluid Flow Group has completed a SEMATECH-sponsored round-robin program to ascertain measurement discrepancies that exist among the gas-flow calibration facilities used in the U.S. Semiconductor Manufacturing Industries (SMI). These calibration facilities provide critical performance data for the mass flow controller (MFC) devices used in semiconductor manufacturing processes.

SMI calibration facilities claim inaccuracies in the range 0.1-0.5%, with the goal to achieve 1% meter performance in process installations. However, reports from MFC users claim performance deviations of 10 to 20 percent or more. In an attempt to resolve this problem,

NIST designed, built, and characterized a gas-flow measurement artifact and test procedure to calibrate the SMI calibration facilities for a selected set of conditions. Nitrogen gas was used for flows in the range from 300 to 800 standard cubic centimeters per minute (sccm). The artifact consists of critical nozzles arranged in tandem to provide redundancy and assurance of performance. The artifact was calibrated at NIST and the calibration data collected was used to specify details of the test procedure. The round robin involved 55 tests performed in 22 laboratories of SEMATECH member companies and related institutions that volunteered to participate.

Results showed that approximately half of the participants had calibration facility inaccuracies of 0.5 percent or less, but approximately one-fourth had inaccuracies of 1 percent or more. Maximum inaccuracies ranged as high as 8 percent. The NIST gas-flow measurement artifact and test procedure are currently being offered as a NIST calibration service that may be requested in the same manner as for conventional flowmeter calibrations. Re-testing this artifact enables participants either to confirm that their initially satisfactory performance is constant in time or to evaluate improvements made in response to initially unsatisfactory results.

Successive phases of this program, currently under development, are expected to extend the flow range to  $0.1-3.0 \times 10^5$  sccm, which is the full range of interest to the semiconductor processing industries. Once the program is completed, the expected significant improvements in SMI gas-flow measurement and control should lead to enhanced productivity throughout these industries.

## 5. Supersonic Inert-Gas Metal Atomization (SIGMA)

P.I. Espina, G.E. Mattingly, F.S. Biancaniello (MSEL), S. Osella (MEL), S.D. Ridder (MSEL), and T.V. Vorburger (MEL)

We continue to participate in a project on Supersonic Inert-Gas Metal Atomization (SiGMA), supported by an industry-government consortium. The objective of this project is to develop a phenomenological model and on-line measurement techniques which can be used with expert systems to optimize this liquid metal break-up and rapid solidification process to produce specific powder characteristics. The SiGMA process is industrially attractive because of its efficiency in producing metal powders with unique micro-structural properties. Such powders improve the strength and corrosion resistant properties of critical components such as turbine blades, valves, bearings, etc.

In the past year CFD studies have conclusively shown how to avoid undesirable gas-flow separation in critical positions in the atomizer and they have shown where improved liquid metal flow arrangements can lead to improved powder size-control. The modeling capabilities developed are efficiently and effectively being transferred to consortium participants through close collaborations and through a three day workshop convened in May 1993. In this way, the consortium members in this program have made very effective use of these modeling capabilities

and industrial production yields have significantly increased according to one member company. Successive phases of this program are expected to demonstrate control of the selected atomization process and complete the transfer of the technology.

## 6. Droplet and Spray Diagnostics

**J.T. Hodges, C. Presser, J.A. Allen, B.L. Shomaker, and J.D. Melvin; G. Gréhan (INSA de Rouen, France), C.M. Megaridis, J. Xin, and J. Day (Univ. of Illinois-Chicago); A.K. Gupta (Univ. of Maryland), C.T. Avedisian (Cornell Univ.), A. Negiz and A. Cinar (Illinois Inst. of Tech.)**

The goal of this program is to develop and apply experimental techniques that provide data needed to elucidate physical phenomena and validate computational models for the interaction of light with single droplets, particles, and spray systems. In addition, the understanding of the dynamics of droplets and particles interacting with gas streams presents an important research challenge in the field of spray combustion and other multi-phase reacting flow technologies. 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.

Fundamental investigations of individual, levitated micron-sized droplets, linear droplet streams and pendant droplets are underway. In a study of light scattering from focused laser beams, measurements have shown that light scattering from droplets is very sensitive to droplet position and laser beam width. As a consequence, many droplet diagnostics that rely on laser-based elastic light scattering phenomena must account for droplet position and beam profile. Our observations have been shown to be well described by generalized Lorenz-Mie theory (GLMT) of light scattering. One consequence of this effort is the observation that the accuracy of phase Doppler systems can be significantly improved by invoking the GLMT to describe the spatial dependence of the phase difference between the measured Doppler bursts.

In a collaborative study of the dynamics of mixing in droplets, a numerical model of internal circulation and multi-component liquid vaporization has been developed at the University of Illinois-Chicago. Three-dimensional internal circulation in spinning droplets has been identified and modeled. Our experimental work, using fluorescence-based visualization on spinning pendant water droplets, is in good accord with the numerical model.

Diagnostic measurements in spray systems have been made to address fundamental phenomena regarding emission of particulates and unburnt droplets into the surrounding environment. Temporal and spatial measurements of droplet size and velocity distributions were carried out using phase Doppler interferometry. The results indicate that droplet transport near the spray boundary is complex and plays an important role in the dispersion of droplets in practical spray systems. Burner design, for example the effects of air swirl induced by the addition of flow

vanes, has been studied in order to establish a rational basis for optimization of firing practice. It was found that a moderate degree of swirl had a positive influence in controlling droplet transport and confining spray structure. These studies are part of a multi-year effort, funded in part by the Department of Energy, to characterize spray flames and improved strategies for optimization of fuel and mixing processes in spray flames.

This year we initiated efforts to investigate the optical and physical properties of multi-phase spray systems. One important application is in the area of spray drying in which vaporization of ceramic laden slurry droplets has a dramatic effect on the material properties of the dried ceramic particles. Therefore, on-line monitoring and control of the vaporization process is potentially of significant interest to the materials industry. Multivariate statistical process control (SPC) techniques have recently been applied by our collaborators at the Illinois Institute of Technology to a commercial spray-drying system. We applied phase Doppler interferometry to characterize the droplet stream and provide initial conditions for development of the SPC schemes. Statistically planned experiments were found to be efficient and effective aids in characterizing complicated relationships between the multiple input and quality parameters and identifying the source of departure from the target operating condition.

#### **7. Physical and Chemical Assessment of Halon Alternatives**

**W.G. Cleveland, G.E. Mattingly, P.I. Espina, C. Presser, J.D. Allen, B.L. Shomaker, D.R.F. Burgess, Jr., M.R. Zachariah, W. Tsang (833), P.R. Westmoreland (Univ. of Massachusetts), B. Breuel, W. Grosshandler, D. Lowe, W. Pitts, W. Rinkinen, and J. Yang (BFRL)**

A major effort was pursued in the areas of flow visualization, chemical kinetic and fluid dynamics modeling, and experimental flame suppression, in support of the Building and Fire Research Laboratory (BFRL) study of potential replacements for the Halon 1301 extinguisher. Twelve gaseous (halocarbon) agents and sodium carbonate, identified by the Wright Research and Development Center (WRDC) as potential extinguishment candidates, were the subject of the study. The results obtained to date are being used in the process of ranking the agents as to replacement suitability and will be further used by the Air Force in the planning of the subsequent full-scale aircraft fire extinguishment evaluation program.

A discharge vessel with observation windows was constructed and used to assess the behavior of all twelve halocarbons and sodium carbonate by high-speed photography and digital-image analysis during three stages of the dispersal sequence: within the storage vessel, during discharge of the agent, and during the process of its interaction with the flame. In addition to the experimental work, the KIVA-II computer code was modified to simulate the flow downstream of an experimental vessel discharging extinguishing agents.

A comprehensive chemical kinetics mechanism has been formulated for gas-phase pyrolysis and oxidation of fluorocarbons. This involved compilation of thermodynamic and chemical kinetic information for all stable and radical halocarbons and oxy-halocarbons; estimation of thermodynamic and kinetic values, where none was available, using empirical and *ab-initio* methods; development of simplified mechanisms through simulations; and modeling of the chemistry at various temperatures, time scales, fuel/oxidizer ratios, and extinguisher concentrations. The chemistry was modeled for different mass-transfer conditions: plug-flow reactor (no diffusion), premixed flame (axial diffusion), and opposed-flow diffusion flame. In the coming year, in addition to serving as a tool for evaluation of the replacement agents, the modeling effort will provide support to experimental studies regarding halon replacement issues in other laboratories (BFRL, WRDC, Naval Research Laboratory, Army Research Laboratory, and Univ. of California at San Diego).

An experimental study is underway to address 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. The facility requirements include high-speed turbulent air flows with varying inlet temperatures, variable fuel and nozzle capabilities, and controlled injection of gaseous and solid agents. Experiments were carried out with two fuels (JP-8 and a hydraulic fluid) under various operating conditions to determine minimum amounts of agents required to extinguish spray flames. The results provided the extinguishment ranking for all candidate agents, which constitutes a crucial criterion for the overall efficiency ranking.

## 8. Chemistry in Supercritical Water Flow Reactors

W.S. Hurst, V.E. Bean, W.J. Bowers, R.W. Davis, E.F. Moore, A. Maček, S.R. Charagundla, J.D. Allen, M.I. Aquino-Class, J.M.H.L. Sengers (838), and W.E. Allman (Babcock and Wilcox, Co.)

This research supports the development of Super Critical Water Oxidation (SCWO) as a process for disposal of industrial wastes and also the development of techniques for *in situ* characterization of high pressure and temperature boiler water.

The optically accessible flow-reactor became fully operational this year upon the installation, characterization and calibration of the optical spectroscopy system and associated computer interfacing. In work under a CRADA with the Babcock and Wilcox company, 27 different organic and inorganic aqueous mixtures (typically at 1 wt% concentration) were characterized successfully by Raman spectroscopy at temperatures of 25, 200 and 300 °C and pressures of 30-35 MPa. This investigation was part of an effort to explore the use of optical diagnostic techniques for monitoring chemicals important in steam and boiling-water power systems. As part of work for the Naval Civil Engineering Laboratory and a CRADA with Conoco, both dealing with treatment of chemical wastes, we demonstrated the destruction of 1,1,1

trichloroethane (TCA) at 200 °C and the destruction of methylene chloride at 300 °C (in water air saturated at 25 °C and with no added oxidant). The destruction of these compounds was inferred from the disappearance of their associated Raman peaks. Ion ( $H^+$  and  $Cl^-$ ) analysis of effluent TCA streams indicates formation of HCl in amounts equivalent to the initial concentration of TCA, confirming the destruction of the compound under these conditions. At temperatures to 350 °C, aqueous mixtures of chlorinated and methylated benzenes were shown to be stable. Diagnostic Raman spectra for the latter mixtures with 5% NaCl/water as the solvent also were obtained. Finally, a technique was developed to make velocity measurements in the flow reactor cell, at about 2% uncertainty. It is hoped that this will form the basis for making *in situ* density measurements which are required for the development and validation of models for the phase behavior of these complex aqueous mixtures.

We have found that engineering models that allow the reliable design of heat exchangers for the insertion or extraction of heat in supercritical water (SCW) flow reactors do not exist. This is because both the flow and heat transfer are greatly affected by the large changes in density and other properties that occur in reaching supercritical temperatures. We have initiated a novel computational simulation of flow and heat transfer through straight tubes inside the SCW reactor. The objective is to acquire an improved understanding of heat exchanger performance in order to better optimize reactor design. The computer simulation is based on the variable density Navier-Stokes equations in conjunction with physical properties obtained from the NBS/NRC steam tables. Various combinations of boundary conditions are applied at the tube wall in order to simulate traversals through heat exchanger configurations. Due to the large variability in the physical properties of supercritical water with temperature, complex heat transfer behavior has been observed. For instance, heating requires longer traversal distances than cooling. Current work focuses on possibly significant buoyancy effects. Experimental measurements for comparison with the predictions are in the planning.

## 9. Chemistry for the Production of High Technology Materials

M.R. Zachariah, M.J. Carrier, C. Amato-Wierda, M.I. Aquino-Class, R.R. Fink, R. Shull (MSEL), and E. Blaisten-Barojas (George Mason Univ.)

Research objectives of this program are the provision of fundamental data, the development and application of process models with associated experimental validation, and the realization of new methods of materials synthesis.

A first principles model for the prediction of nucleation kinetics for ceramic particles has been developed. Formation of  $SiO_2$  from the vapor was used as prototype system. To provide the fundamental data necessary to describe nucleation, we applied *ab-initio* molecular orbital theory to obtain the most stable equilibrium structure for small clusters. Transition state computations and application of RRKM theory allowed the determination of the rate constants for dimer, trimer, and tetramer formation as a function of temperature and pressure. In addition, reaction



rate constants for cluster oxidation from water vapor have been calculated in an attempt to qualitatively explain the behavior, seen by a number of research groups, that cluster oxidation is slower than cluster growth. When incorporated in detailed chemical kinetic models for particle growth, the new mechanisms, studied in this work, result in substantially slower nucleation rates than those typically employed for the simulation of particle formation. The data and models developed in this research have special application to the early stages of nanoparticle synthesis, as well as the formation of contaminant particles formed during CVD.

In an attempt to understand the chemistry of cluster growth and cluster-cluster interactions, we utilize molecular dynamics (MD) simulations. This year, MD simulations for silicon cluster growth up to 1000 atoms have been made. While the simulations constitute a data base of cluster growth kinetics as a function of cluster size and temperature. While the analysis of the results is ongoing, preliminary findings can be summarized as follows: (1) cluster-cluster collision kinetics show the rates to be gas-kinetic, in contrast to the much lower rates found for small clusters (as discussed above); (2) equilibrium cluster potential energy shows surprisingly weak sensitivity to cluster size and a  $T^{0.5}$  dependence on cluster temperature; (3) phonon spectra show behavior very similar to the bulk; (4) the characteristic times for coalescence of the colliding clusters is very sensitive to both temperature and cluster size; and (5) atom-mixing is much slower than particle coalescence. Engineering correlations are currently being derived from the results of these simulations.

This year we have instituted a joint project with the Materials Science and Engineering Laboratory at NIST to develop a method for the generation of bulk quantities of a superparamagnetic nanocomposite. The process involves vapor phase generation of nanometer magnetite ( $\text{Fe}_3\text{O}_4$ ) particles within a ceramic host (silica). Preliminary results, as characterized by transmission electron microscopy and Mossbauer spectroscopy, have confirmed that we are able to synthesize structures that show superparamagnetic behavior and iron oxide encapsulation.

In support of an ATP program recipient (Nanophase Technologies) we have formed a CRADA to provide assistance in the implementation of *in-situ* characterization of their nanoparticle production facility. A light scattering apparatus for characterizing the behavior of their reactor has been loaned to the CRADA partner. At present the diagnostic is being employed to obtain information on the stability of the reactor. Future developments are aimed at the design of a new viewing chamber to enable a more robust application of the diagnostic.

#### 10. Self-Assembled Monolayers for Biosensing

**M.J. Tarlov, M.E. Collison, G.E. Poirier, D.R.F. Burgess, Jr., A.L. Plant (831), and J.G. Gillen (837)**

The research effort in self-assembled monolayers (SAMs) is directed towards development of these systems for chemical and biological sensing applications. The project is focussed on the

alkanethiol SAMs of the general formula  $X(\text{CH}_2)_n\text{SH}$ , where X is chosen from a wide variety of functional groups or molecules, and n ranges from 1 to 20. The thiol headgroup (-SH) adsorbs strongly on a variety of surfaces (Au, Ag, Cu, Pt, GaAs) to form densely packed, crystal-like assemblies yielding a surface comprised of the terminal functional group, X. By varying the identity of X, the surface chemical and physical characteristics can be customized to control adsorption processes and impart chemical recognition properties to SAMs. Work this year concentrated on: (1) a versatile SAM photopatterning method for the construction of miniaturized chemically sensitive arrays; (2) development of generic methods of attaching biological reagents to SAMs using biotin-avidin coupling chemistry; and (3) molecular resolution characterization of SAMs with scanning tunneling microscopy (STM).

Nanometer-level manipulation of the monolayer properties perpendicular to the surface is easily attained by varying the chain length and terminal functional group. There is also a need for precisely controlling the position of alkanethiol molecules in the plane of the surface to enable the patterning of biological reagents on solid supports for multi-component sensing arrays. To this end, a versatile, simple method to photopattern SAMs was developed this year. In the process, an alkanethiol SAM is irradiated with UV light through a mask. The alkanethiolates are photo-converted to alkanesulfonates in the exposed areas, while the thiolates remain unchanged in the unexposed areas. The sample is then immersed in a solution of a second alkanethiol, thereby displacing the weakly bound sulfonate species. This results in a single monolayer film comprised of two different alkanethiol molecules in a pattern determined by the mask. Compositional maps of the patterned SAMs were obtained using secondary ion mass spectrometry (SIMS) imaging in collaboration with the Surface and Microanalysis Science Division (837). SIMS images demonstrate the successful formation of patterned, two component SAMs and the writing of features as small as  $10\ \mu\text{m}$ . A patent for the photopatterning process has been submitted. Experiments are in process to demonstrate the utility of patterned SAMs for directing the adsorption of proteins.

For SAMs to be useful in sensing applications, simple, generic methods for immobilizing biological molecules on SAM surfaces at high coverage and full activity are highly desirable. Our strategy is to exploit the specific binding of biotin, (a vitamin), to avidin, (a protein found in egg whites). Each avidin can bind up to four biotin molecules and, thus, can be used as a bridging structure or "molecular glue" to immobilize a host of biotin-labeled proteins. Investigations this past year have examined the adsorption of avidin on SAMs with carboxyl, perfluorinated, and biotin terminations. As expected the perfluorinated termination prevented protein adsorption, a functionality which is required for the fabrication of arrays. The effectiveness of the perfluorinated layer in preventing adsorption may also have implications for suppressing non-specific protein binding in biosensors and to issues of biocompatibility in general. The carboxyl and biotinylated terminations show a high propensity to bind the avidin protein. Ellipsometry and contact angle measurements show almost complete coverage with approximately monolayer thickness of the protein. Unfortunately, the avidin so adsorbed appears to have low activity for binding additional biotin. We are currently exploring the

possibility that this loss of activity is associated with steric hindrances and will employ a biotinylated alkanethiol with a longer spacer arm in an effort to minimize these hindrances.

The ability to manipulate and exploit the properties of alkanethiol SAMs for sensing applications will depend in part on molecular-level understanding of these assemblies. Recently acquired STM images have provided exciting glimpses of the rich variety of structures that are formed by the adsorption of alkanethiol molecules on Au(111) single crystals. Unlike previous STM studies, simple, hexagonally packed arrays corresponding to a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure are not observed. Instead,  $(\sim 10 \times \sqrt{3})$  monolayers are observed for hexanethiol and butanethiol SAMs, while a  $(4\sqrt{3} \times 2\sqrt{3})R30^\circ$  monolayer is observed for decanethiol. The differences in the monolayer structures are attributed to the increasing importance of chain-chain interactions in the longer chain decanethiol SAMs. In addition, domain sizes of over 10 nm are observed for the ordered overlayers along with clearly resolved domain boundaries. STM experiments on SAMs will be important for characterizing the structure of biological reagents immobilized on SAM surfaces.

## 11. Gas Sensing with Ultrathin Films

S. Semancik, R.E. Cavicchi, G.E. Poirier, V.Y. Sukharev (Guest Researcher), and M. Gaitan (EEEL), and J. Suehle (EEEL)

A primary goal of our interdisciplinary program on chemical sensing is to develop the science and technology for producing a new generation of faster, more versatile and more reliable gas sensors. While many different solid state sensing principles can be applied, our effort focuses on gas-induced conductance changes in semiconducting oxide-based materials, such as tin oxide ( $\text{SnO}_2$ ). This approach combines the use of robust, high quality materials with a conductance-based device concept which is readily amenable to incorporation into sensing arrays. The effort is aimed at providing commercializable, generic technology that can impact a number of large market areas, e.g., industrial process control, pollution prevention, and environmental monitoring. The results from this project were presented at the NIST Workshop on Gas Sensors, held September 8-9 at NIST and organized by the Process Sensors Group, and at other national meetings, and have generated considerable interest by a number of sensor manufacturers.

Research this year focused on investigating response characteristics of very thin films of  $\text{SnO}_2$  having excellent crystallinity. Using reactive sputter deposition, crystal-like films of (100) and (101)  $\text{SnO}_2$  were fabricated on sapphire substrates. The use of low-energy electron diffraction (LEED) and probe microscopies (STM, AFM) has verified the extremely high film quality for both crystalline orientation and smoothness (0.3 nm rms over  $4 \mu\text{m}^2$ ). The level of perfection in the growth process has allowed layer-by-layer deposition of continuous films down to thicknesses as little as 1.5 nm, i.e. only 5 atoms thick.  $\text{SnO}_2$  films of 1.5, 4.0 and 8.0 nm thicknesses were used to systematically investigate ultrathin film gas sensing. Pd islands,

approximately one monolayer thick, were surface-dispersed on these specimens to investigate catalytic enhancement effects on sensing response. The entire range of oxide film thicknesses down to 1.5 nm gave a sensing response. Moreover, the initial data in these experiments suggest that the most reproducible responses were measured from the 1.5 nm film. This result is consistent with the underlying rationale for developing ultrathin films as a means for assuring reliable, repeatable gas sensing devices. This year our largely experimental program has been combined with a theoretical effort addressing the effects of depletion regions, formed under metal islands, on film conductivity. New insights into the importance, relative to the "spillover" mechanism, of the contributions of subsurface depletion to the sensing response have resulted from this analysis.

The film growth and gas sensing technological capabilities of the Process Sensing Group have been combined with those in silicon micromachining and integrated circuit fabrication of the Semiconductor Electronics Division (EEEL) with the objective of developing a new approach to gas sensing technology. CMOS (complementary metal oxide semiconductor) fabrication provides the means to develop multi-layer, suspended array structures capable of achieving controlled temperatures up to approximately 800 °C. These are envisioned as the basis for conductometric gas sensing arrays comprised of pixels having individually controllable sensing response characteristics combined with on-chip electronic processing. Combining thermal programming techniques with catalytic metal surface additives enhances response characteristics and selectivity of sensing arrays. The thermal programming capability of micromachined structures has been combined with SnO<sub>2</sub> film deposition to investigate sensing response of such structures with and without monolayer-regime, catalytic metal overlayers. Thermal programming techniques are being adapted for low power consumption in sensing arrays. Characterization of sensing response to a broader range of gases has been initiated with the completion of a sensor test cell. This cell provides the means to determine response databases for subsequent training of artificial intelligence algorithms to decipher array response patterns in multi-component gas sensing. Future efforts in this project will focus on the development of overlayer deposition methods for sensing and catalytic metal overlayers on single pixels or groups of pixels in an array, development of robust sensing-film electrical contacts, and addition of on-chip electronic circuitry.

## 12. Processing For Electrically Conductive SiC Thin Films

**K.G. Kreider, D.R.F. Burgess, Jr., M.J. Tarlov, and N. Quick (Applicote Associates)**

Silicon carbide has excellent physical and electronic properties for use in devices in preference to silicon or GaAs when high temperatures or high power densities are required. Using SiC a variety of devices with promising characteristics have been demonstrated in the areas of blue and UV optoelectronics, high temperature electronics, high-power/high-frequency devices, and nonvolatile electronics. Although conventional metallization techniques can be used for these

devices, it would be very useful if low cost techniques were developed which would overcome the limitations of standard metallization techniques. We have investigated a direct laser conversion technique to create electrical conductors on high band-gap, silicon carbide thin films.

Thin films of silicon carbide (SiC) were sputter-deposited on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and Si substrates using a SiC target with an RF planar magnetron. These films were irradiated with multiple 15 ns pulses (1-100) at 308 nm from an excimer laser (XeCl) creating 1-2 mm wide electrically conducting paths. The electrical conductivity of both the non-irradiated and irradiated films was evaluated as a function of substrate type, deposition temperature, surface appearance, surface stoichiometry, annealing temperature, sputter gas composition, film thickness and laser processing conditions (energy and power per unit area). In one case, irradiation lowered the resistivity of the film, originally 10<sup>3</sup> Ω-cm, to 160 μΩ-cm. This compares to a value of 50 μΩ-cm obtained after irradiating bulk SiC using the processing technique developed by our CRADA partner, Applicote Associates. We have applied X-ray photoelectron spectroscopy, secondary ion mass spectrometry, Auger spectroscopy, X-ray diffraction, scanning electron microscopy, and Raman spectroscopy among other diagnostic techniques in order to characterize these samples. We were thus able to characterize both the unexposed films and the conducting traces formed in the films by UV-laser irradiation, as to their composition, surface oxide, critical binding energies, lattice structure, and morphology of the microstructure. Models for the phase transformations and the conductivity resulting from laser treatment have been formulated. A paper describing these results is in preparation.

### 13. Implementation of New International Temperature Scale of 1990 (0.65 K - 1235 K)

C.W. Meyer, M.L. Reilly, W.L. Tew, G.W. Burns, M.G. Scroger, G.F. Strouse, D.C. Ripple, G.T. Furukawa (Guest Researcher), B.W. Mangum, H. Nubbemeyer (PTB, Berlin), and J. Lin (CMS/ITRI, Taiwan)

Until the new facilities for realizing the ITS-90 (and for calibrating customer thermometers below 83.8 K) are completed, the NIST-ITS-90 low-temperature "wire scale", which serves as the NIST reference for calibrations in the region 0.65 K to 83.8 K, is being maintained and used. This scale consists of two distinct wire scales: a standard platinum resistance thermometer (SPRT) based scale, spanning the region 13.8 K to 83.8 K and used primarily for calibration of SPRTs, and a rhodium iron resistance thermometer (RIRT) based scale, spanning the region 0.65 K to 27.1 K and used primarily for calibration of RIRTs and germanium resistance thermometers (GRTs). Once we realize the ITS-90 as it is defined in this range of temperature, it will replace the NIST-ITS-90 wire scale. That change will reduce the uncertainty of calibrations.

The construction of the new facilities for realization of the ITS-90, as defined, below 84 K is essentially complete. The facility for realizing the ITS-90 below 25 K will provide primary calibrations for "in-house" capsule-type SPRTs and RIRTs which subsequently, in the new

calibration facility, will be used to transfer the ITS-90 to the user community. In this scale-realization apparatus, we will incorporate the five fixed points which define the ITS-90 between 0.65 K and 24.5561 K (plus possibly the ITS-90 fixed points at 54.3584 K and 83.8058 K). The facility will use  $^3\text{He}$  and  $^4\text{He}$  vapor-pressure thermometry for the realization of temperatures between 0.65 K and 5.0 K, and  $^3\text{He}$  or  $^4\text{He}$  interpolating constant-volume gas thermometry for realization of temperatures between 3.0 K and 24.5561 K. This requires instrumentation and measurement capability which were not necessary for the previous scale. To achieve an inaccuracy in temperature of not more than 0.1 mK, the pressure must be measured with an inaccuracy of less than 30 ppm (vapor pressures) and with an imprecision of less than 3 ppm (gas thermometry). We measure these pressures with a gas-lubricated piston gage in series with a differential capacitance diaphragm gage. Operation of the measurement system over an extended range was successfully demonstrated this year by measuring the triple-point temperatures of commercial grade Ar (84 K),  $\text{O}_2$  (54 K) and Ne (25 K). Also, diode thermometers were calibrated over the range 1 K to 300 K and then installed in the apparatus for measurement of the temperature profile of the filling-tube assembly. That information is essential for accurate vapor-pressure and gas thermometry. Preliminary measurements with the interpolating constant-volume gas thermometer, using  $^4\text{He}$  as the working fluid, also have been conducted successfully between 13 K and 25 K.

As part of our effort to ascertain how closely our realization of the ITS-90 agrees with those of other nations, we have intercompared freezing-point temperatures of our Ag fixed-point cells with those of the German (PTB) and Taiwan (CMS/ITRI) national laboratories. The work was performed during the tenure of Guest Researchers from those laboratories. Three PTB Ag cells and one CMS Ag cell were directly compared with NIST cells, the resolution being better than 0.1 mK. In all cases, the NIST reference cell was of higher quality, as judged on the basis of freezing-point temperatures, than those from PTB and CMS. These comparisons among the participating laboratories established agreement of the national realizations of the ITS-90 and indicate the possibility of further refinements in the accuracy of realizations of the scale. Additionally, a triple point of water cell from the Netherlands national laboratory (VSL) was compared with one of our triple point of water cells. Their cell was of a somewhat lower quality than our cell, the temperature of the VSL cell being 0.14 mK lower than that of the NIST cell.

Since there are no systematic data on the non-uniqueness of the ITS-90 in the range 631 °C to 962 °C, and since such data also are sparse in the range 20 °C to 630 °C (at the levels of precision that can be achieved with modern measurement equipment), precise comparison data of SPRTs in these ranges of temperature are needed to determine the limitations of the ITS-90. Comparison experiments to obtain such data also are required to establish realistic uncertainty statements for calibrations. Consequently, we have planned and organized a new international effort to determine these limits of accuracy. To adequately determine the non-uniqueness in any range of temperature a large sample of SPRTs is required. This collaborative effort with the national laboratories of Italy (IMGC) and the Netherlands (VSL) will involve up to 30 HTSPRTs contributed by the three participants. Each participant will calibrate its HTSPRTs, and IMGC

and NIST will calibrate and intercompare all 30 thermometers over a wide range of temperatures with a special focus on the region from 631 °C to 962 °C.

#### 14. High Temperature Thermometry Research

G.W. Burns, D.C. Ripple, G.F. Strouse, G.T. Furukawa, B.W. Mangum, J. Valencia-Rodriguez (CENAM, Mexico), and V. Marinez-Fuentes (CENAM, Mexico)

The central focus of the research in this area is the thermocouple. A major accomplishment this year was the publication of NIST Monograph 175, entitled "Temperature-Electromotive Force Reference Functions and Tables for the Letter-Designated Thermocouple Types Based on the ITS-90." This work presents reference functions and tables based on the ITS-90 for the eight, ISA letter-designated thermocouple (TC) types: noble-metal types B, R and S, and base-metal types E, J, K, N and T. The more-than-600-page manuscript contains 118 tables, giving values of temperature and electromotive force in several different formats to satisfy the requirements of various users. This monograph is the defining document for thermocouple thermometry for industrial and calibration laboratories both in the U.S. and throughout the world.

Studies of the emf stability and repeatability of Pt/Pd TCs for different methods of annealing and for wire of different purity were begun. This is part of our effort to develop new TCs as reference thermometers and as fairly-inexpensive, high-stability, high-temperature thermometers for industrial use. Another part of this effort is the evaluation of new thermometric sensors, and in this area, an apparatus to provide both accurate calibrations and measurements of the long-term drift of thin-film thermocouples (TFTCs) was designed and appropriate instrumentation ordered. Investigations of these TFTC sensors will begin in FY94.

As part of a collaboration with CENAM, five Au/Pt thermocouple thermometers were constructed using high-purity (99.999+%) Au and Pt wires. Each of the TCs was calibrated at the freezing points of Ag, Al, Zn, Cd, Sn and In, using the freezing-point cells and furnaces in the NIST Platinum Resistance Thermometry Calibration Laboratory. Immersion tests in the Ag and Al freezing-point cells showed each of the TCs to be highly homogeneous. The deviations of the fixed-point data for these TCs from the NIST Au/Pt TC reference function were less than the equivalent of 25 mK over the entire range of temperature. The deviations for each TC were fitted with a 2nd degree polynomial by the method of least squares.

## 15. Thermometric Fixed Point Development

B.W. Mangum, G.F. Strouse, G.W. Burns, D.C. Ripple, M.G. Scroger, and J. Valencia-Rodriguez (CENAM, Mexico)

In recent years we have had a significant effort in developing fixed point cells with the goal of disseminating the ITS-90 to secondary calibration laboratories. In this effort, the melting/freezing behavior of three Ag freezing-point cells, constructed in FY92 using 99.9999+ % pure Ag, was evaluated as part of the certification process of the high-purity Ag for use as Standard Reference Material (SRM) 1746, the Silver Freezing-Point Standard. The freezing-point temperatures of the three Ag cells (961.78 °C) were highly reproducible and agreed to within 0.1 mK. Other features of the melting/freezing curves also indicated the Ag to be of extremely high purity. SRM 1746 is now available for purchase. Also, as part of this effort, the melting/freezing behavior of three Al freezing-point cells containing 99.9999+ % pure Al is being investigated to complete the certification process of high-purity Al to serve as SRM 1744, the Aluminum Freezing-Point Standard at 660.323 °C. This work will be completed in FY94.

Certifications of SRM 1972 (Ethylene Carbonate) and SRM 1973 (n-Docosane) Triple-Point Standards (with triple-point temperatures of 36.314 °C and 43.879 °C, respectively) were completed. These SRM mini-cells were purified by zone-refining techniques at Rensselaer Polytechnic Institute and certified at NIST. They will be of primary use in medical/biomedical applications but are also useful for general calibrations of small sensors.

In our collaboration with CENAM, two Al and two Zn freezing-point cells, each containing 99.9999% pure metal, have been constructed and evaluated for the Thermometry Group of CENAM. These were found to be metrological-quality cells with the temperatures of the Al and Zn cells lower than those of the corresponding NIST standards by only 0.6 mK and 0.4 mK, respectively.

One Zn and three Al freezing-point cells, each containing 99.9999% pure metal, were constructed and evaluated for use in our Platinum Resistance Thermometer Calibration Laboratory. Additionally, two Zn, two Al, one Ag and one Sb freezing-point cells, each containing 99.9999% pure metal, were constructed and found suitable for use in the Thermocouple Calibration Laboratory.



## 16. Heat and Mass Transfer in Cryogenic Systems

P.J. Giarratano, M.A. Lewis, D.A. Olson, J.D. Siegwarth, M.C. Jones (830) and N. Van Dresar (NASA/Lewis)

Liquid hydrogen will moderate the neutron beam and provide refrigeration in the upgrade of the NIST Cold Neutron Reactor Facility (CNRF) operated by the Materials Science Engineering Laboratory. Designers expect the modification to enhance the flux of neutrons at the desired wavelength by a factor of 5 to 7 over that obtained with the present cold D<sub>2</sub>O-ice moderator. In a project begun last year at the request of CNRF design engineers, we have constructed a full-scale mock-up of the hydrogen moderator and thermosyphon flow loop to determine the functionality and stability of the proposed design. The radiation heat load was simulated with electric heaters. This year's experimental results on the mock-up demonstrated that the liquid hydrogen circulation was self-regulating and stable at heat inputs from 500 to 2200 watts (800 watts is the expected heat load) and that the resulting void fraction was well below the maximum acceptable 20%. Difficulties with restart after flow stoppage, intended to simulate a temporary interruption in the CNRF helium refrigerator, were encountered in the experimental mock-up. A modification to the experimental apparatus to extend the liquid fill line to the bottom of the moderator chamber improved the restart performance; however, reliable restart only occurred at low power inputs and after short periods without liquid flow. The final CNRF system is designed to favor easier restart for the actual system. Our test results were documented in a final report to CNRF design engineers.

The success of the hydrogen moderator experimental study for the CNRF led to a request for a similar study from Oak Ridge National Laboratory (ORNL). ORNL plans to build an Advanced Neutron Source (ANS) where liquid deuterium is circulated through a spherical aluminum vessel to remove heat and moderate the neutron beam. We conducted a preliminary study for a research program to provide data and/or models to determine the heat transfer mechanisms and predict performance of the ANS cold neutron moderator cooling system. An experimental apparatus to obtain basic, flat-plate forced convection deuterium heat transfer data and to simulate the ORNL spherical moderator and coolant pumped flow system was designed. Thermodynamic and transport properties for deuterium were assembled and utilized in classical forced convection boiling heat transfer correlations. We calculated wall temperatures and void fractions for various heat loads, degrees of subcooling, and flowrates. The calculations will be used for comparison with experimental data obtained from test systems developed by NIST in a second phase of the project.

The management of heat and mass transfer in cryogenic fluids is also extremely important in aerospace applications. For example, NASA must develop technologies for controlling pressure in orbiting cryogenic liquid hydrogen tanks. A concept under consideration for this is the Thermodynamic Vent System (TVS). As pressure builds up in the tank due to heat leaking into it, a sacrificial amount of liquid in the tank flows through a Joule-Thompson valve and enters a heat exchanger tube submerged in the bulk fluid. The Joule-Thompson expansion causes a

temperature drop in the fluid providing a temperature difference to remove heat from the storage tank with a consequent drop in pressure. The liquid in the tube vaporizes as it flows through the tube, changing from mostly liquid to saturated vapor or possibly superheated vapor at the outlet vent. The heat transfer rate to the vaporizing 2-phase flow must be known to effectively design the TVS. The expected heat flux and mass flow conditions are much lower than can be confidently extrapolated from existing data bases. Therefore, with funding from NASA/Lewis, we built an experimental apparatus to simulate the TVS conditions and generate the data and information required to understand and predict the heat transfer behavior. This year we initiated tests using liquid nitrogen. The first results suggest that some modifications are required to produce the best simulation. Design correlations are expected to be generated in the coming year.

#### 17. Advanced Refrigeration for Superconductivity Applications

R. Radebaugh, P.E. Bradley, E.D. Marquardt, W. Rawlins and K. Kapkin (Univ. of Colorado), and J. Gary and A. O'Gallagher (CAML)

This program has a number of major elements focussed on technology-enablers for cryocoolers: cryogenic refrigerators and their associated regenerators, and compressors. The principal focus of the cryogenic refrigerator effort is the orifice pulse tube refrigerator. Two major projects are underway: one collaborative with Tektronix and the other one conducted on behalf of the Naval Surface Warfare Center.

The Tektronix project is part of their larger program to develop a system for high-speed digital communication utilizing NbN superconducting electronics. The overall program is being funded by ARPA. NIST and Los Alamos National Laboratory (LANL) are under subcontract to Tektronix through CRADAs to help them develop the thermoacoustically driven orifice pulse tube refrigerator (TADOPTR) for this application. The TADOPTR has no moving parts, which gives it the potential for extreme reliability and low manufacturing cost. The refrigerator uses a heat-driven thermoacoustic driver (TAD), being developed with LANL assistance, to drive an orifice pulse tube refrigerator (OPTR) which we are developing. Together with LANL we demonstrated several years ago that a 30 Hz TADOPTR could achieve 90 K with a one stage OPTR. The goal of this four year program with Tektronix is to reach 10 K using a four stage OPTR. In addition, in order to miniaturize the refrigerator, operating frequencies first of 100 Hz and then 400 Hz are to be used.

Progress during this year included improving our modeling and analysis techniques for multiple stage pulse tubes and regenerators; expansion of our regenerator analysis code, REGEN3.1, to include additional information regarding the entropy production and lost work associated with pressure drop in regenerators; and design of a four stage 100 Hz OPTR based upon our best estimates of pulse tube efficiencies from previous measurements at much lower frequencies. We also prepared detailed drawings for a test apparatus and for the first stage of the OPTR. These

parts were fabricated by Tektronix (under our supervision) in order to transfer the OPTR technology to Tektronix as part of the CRADA. At the close of the year, a 100 Hz TAD with a one stage OPTR was turned on for the first time at Tektronix and achieved 195 K with 70% of full power supplied to the TAD. The results are currently being compared with theoretical predictions. Some improvements will most likely be needed. We received a similar 100 Hz TAD manufactured by Tektronix and will repeat the Tektronix tests as a check for reproducibility. Our next focus will be on testing of the third and fourth stages, while Tektronix continues work on the first and second stages.

The second project in orifice pulse tube refrigerators, which is being funded by the Naval Surface Warfare Center, has a goal to demonstrate that a pulse tube refrigerator can achieve a temperature of 4 K. The Navy's interest is to cool a superconducting magnet for mine sweeping. The lowest temperature achieved previously with a pulse tube refrigerator was 11.5 K. This refrigerator is to be driven with a mechanical compressor that can provide a pressure ratio of at least 2 and operate at a low frequency of 2 Hz. Most of this year's effort involved the modeling of the last stage regenerator, which is to operate in the region of 4 to 15 K. The operating fluid, helium, is in the supercritical phase in most of the regenerator, and modeling at 4 K required several modifications to our existing modeling code REGEN3.1. Studies were done to find the optimum operating conditions, such as average pressure, pressure ratio, and temperature of each stage. Modeling and optimization of all three stages of regenerators has been the focus of these initial efforts.

We have numerous interactions with the private sector in the area of cryogenic refrigeration. This year's efforts included a systems analysis for BEI Electronics. This company is interested in developing a commercial pulse tube refrigerator to be used for cooling high temperature superconducting electronic circuits. The refrigerator was to provide 5 W of cooling at 77 K and be able to use their existing compressor that had a swept volume of 7 cm<sup>3</sup>. We completed the design and analysis of the entire system, including the regenerator, pulse tube, orifices, and the three heat exchangers. We also did an analysis of their existing Stirling refrigerator and made some recommendations to them that could improve its performance.

Our efforts in the development of new regenerator materials for cryocoolers have two essential parts: (1) the measurement of regenerator performance with different materials and configurations for the temperature range of 77 K to 300 K, and (2) the development of new materials and configurations for regenerators operating at temperatures below 40 K. These regenerators would be used in cryocoolers such as the Stirling, Gifford-McMahon, or pulse tube types. In support of the first area, we have developed a hot-wire technique for measuring oscillating mass flow at cryogenic temperatures. We have applied this technique to measurements of instantaneous mass flow and temperature within a pulse tube refrigerator. This type of measurement provides much needed data on energy flows in a pulse tube and regenerator for validation of refrigerator and regenerator modeling and design efforts. We also have constructed and are in the process of testing a new apparatus for the measurement of regenerator materials below 40 K. This is part of our effort, joint with the University of Colorado, to

develop new regenerator materials. Methods for depositing high heat capacity materials like  $\text{Er}_3\text{Ni}$  onto various substrates have been explored using many of the facilities available at the university. Sputtering, evaporation, and laser ablation are under investigation.

The final element of the refrigeration program is the development of design methodology for highly efficient linear-resonant compressors or pressure oscillators to be used to drive pulse tube or Stirling cryocoolers. As part of this work, a set of design equations and scaling laws have been developed and published this year. An optimization procedure also was developed for the flexure springs that are used in such compressors to eliminate all rubbing contact. A set of flexure springs were fabricated and the radial and axial stiffnesses were measured. The results agreed with our nonlinear finite element modeling results to within about 5%. In a future continuation of this program, a laboratory compressor, for which we have completed detailed design drawings, is to be constructed. This system will be used for studies of these linear-resonant systems and for development of an entire pulse tube refrigerator system based on this type of compressor. The work is being funded by NASA/Ames.

C. **Outputs and Interactions**  
(Process Measurements Division)

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- Scott, J.L., "Comparing NIST-B 50 mm Orifice Meter Gas Data to the ANSI Equation," in Proc. of ASME Conference on Fluid Measurements, ASME Fluid Measurement and Instrumentation Forum, FED-161, 13 (1993).

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- Semancik, S. and Cavicchi, R.E., "Development of Tailored Films and Surfaces for Use in Advanced Chemical Sensors," in Materials Research Society Symposium on Smart Devices Microelectromechanical Systems 276, 137-148 (1992).
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- Strouse, G.F. and Mangum, B.W., "NIST Measurement Assurance of SPRT Calibrations on the ITS-90: A Quantitative Approach," in Proc. of the 1993 Measurement Science Conference, Session 1-D (1993).
- Strouse, G.F., Furukawa, G.T., and Mangum, B.W., "Preliminary Results of a Comparison of Water Triple-Point Cells Prepared by Different Methods," BIPM Com. Cons. Thermométrie 18, CCT/93-24 (1993).
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- Tew, W.L. and Mangum, B.W., "New Procedures and Capabilities for the Calibration of Cryogenic Resistance Thermometers at NIST," *Advances in Cryogenic Engineering* **39** (in press).
- Tew, W.L. and Williams, E.R., "A Flux Locked Current Source Reference," *IEEE Transactions on Instrumentation and Measurement* **42**, 186-190 (1993).
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- Zachariah, M.R. and Tsang, W., "Ab Initio Computation of Thermochemistry and Kinetics in the Oxidation of Gas Phase Silicon Species," in Proc. of MRS in Chemical Prospective of Microelectronics Materials III **282**, 493 (1993).
- Zachariah, M.R., "Application of Ab-Initio Molecular Orbital and Reaction Rate Theories to Nucleation Kinetics," *Aero. Sci. & Tech.* (in press).

## 2. Talks

- Bean, V., "Transient Pressure Measurement and Calibration," Measurement Science Conference, Anaheim, CA, January 22, 1993. Invited
- Bean, V.E., Bowers, Jr., W.J., Hurst, W.S., and Rosasco, G.J., "A Primary Standard for Dynamic Pressure and Temperature," Second International Pressure Symposium, Paris, France, June 4, 1993. Invited

- Bean, V.E., "Dynamic Pressure Metrology," Second International Pressure Symposium, Paris, France, June 4, 1993. Invited
- Bean, V.E., "Two-day short course on Pressure Metrology and its Industrial Applications," Centro Nacional de Metrologia (CENAM), Mexico City, Mexico, September 27-28, 1993. Invited
- Bradley, P.E., "Energy Flows in an Orifice Pulse Tube Refrigerator," Cryogenic Engineering Conference, Albuquerque, NM, July 15, 1993.
- Burgess, Jr., D.R.F., "Reaction Pathways and Reduced Mechanisms for Silane Pyrolysis and Oxidation," AIChE Symposium on High Temperature Processing of Materials, Miami Beach, FL, November 2, 1992.
- Burgess, Jr., D.R.F., "Transient Thermal Response of Thin Film Thermocouples Used as Heat Flux Probes in Ceramic Lined Internal Combustion Engines," AIChE Symposium on Fundamental Research in Heat Mass and Momentum Transfer, Miami Beach, FL, November 5, 1992.
- Burgess, Jr., D.R.F., "Reaction Pathways and Reduced Mechanisms for Oxidative Destruction of Organic Wastes," AIChE Symposium on Oxidative Destruction of Hazardous Wastes, Miami Beach, FL, November 6, 1992.
- Burns, G.W., "Gold Versus Platinum Thermocouples: New High-Accuracy, High-Stability Transfer Standard at Temperatures up to 1000 °C," ASTM Committee E-20 Colloquium, Kiawah Island, SC, November 11, 1992. Invited
- Cavicchi, R.E., and Semancik, S., "Surface and Film Properties of SnO<sub>2</sub> and Applications for Micromachined Structures," AFOSR Contractors' Meeting, Washington, D.C., October 27, 1992.
- Cavicchi, R., "Custom Surfaces for Planar Solid State Gas Sensors," American Vacuum Society 39th National Symposium, Chicago, IL, November 11, 1992.
- Cleveland, W.G., "Liquid Density Measurement Using the Buoyant Force Method," 1993 Measurement Science Conference, Anaheim, CA, January 22, 1993.
- Cleveland, W.G., "Air Speed Measurement Techniques at the National Institute of Standards and Technology," ASHRAE 1993 Winter Meeting, Chicago, IL, January 27, 1993. Invited
- Collison, M.E., "Design of Biosensor Interfaces Using Molecular Self-Assembly Phenomena," American Chemical Society, Chicago, IL, August 26, 1993.

- Davis, R.W., "Numerical Modeling of Particle Dynamics in a Rotating Disk CVD Reactor," AIChE Symposium on Transport Processes in Electronic Materials, Miami Beach, FL, November 3, 1992.
- Espina, P.I., "Numerical Investigation of the Compressible Flow Field Produced by an Annular Jet Close-Coupled Gas-Metal Atomizer," TMS Fall Meeting, Chicago, IL, November 2, 1992.
- Espina, P.I., "Study of an Underexpanded, Annular Jet Past an Asymmetric Backward-Facing Step," Dissertation Proposal Seminar, Department of Mechanical Engineering, University of Maryland, College Park, MD, February 3, 1993.
- Espina, P.I., "The Evolution of Gas-Metal Atomization: From Discrete Jets to Annular Jets Via Computational Fluid Dynamics," Third International Conference on Powder Metallurgy in Aerospace, Defense and Demanding Applications, San Diego, CA, February 9, 1993.
- Espina, P.I., "CFD Results for the Gas-Only Flow in Selected Atomizer Geometries," SiGMA Consortium Meeting, NIST, Gaithersburg, MD, March 31, 1993.
- Espina, P.I., "Process Modeling for SiGMA," SiGMA Consortium Meeting, NIST, Gaithersburg, MD, March 31, 1993.
- Espina, P.I., "Flow Research Results from SiGMA Studies," NIST, Gaithersburg, MD, April 7, 1993.
- Espina, P.I., "Flow Modeling of the Gas-Metal Atomization Process," NIST, Boulder, CO, July 21, 1993.
- Espina, P.I., "Parameterization of the Gas-Metal Atomization Process," SiGMA Consortium Meeting, NIST, Gaithersburg, MD, September 22, 1993.
- Gupta, A.K., "Droplet Transport in a Swirl-Stabilized Spray Flame," 8th Int'l Conf. for Mechanical Power Engineering, Cairo, Egypt, April 27-29, 1993.
- Hess, D.E., "Measurements of the Stable Response of a Passive Compliant Surface to Bursts in a Turbulent Boundary Layer," 45th Annual Meeting, Division of Fluid Dynamics, American Physical Society, Florida State University, Tallahassee, FL, November 24, 1992.
- Hess, D.E., "Recent Velocity and Displacement Measurements Detailing the Interaction of a Passive Compliant Surface and a Turbulent Boundary Layer," Forum on Turbulent Flows, Fluids Engineering Conference, American Society of Mechanical Engineers, Washington, DC, June 21, 1993.

- Hodges, J.T., "Elastic Scattering from Spheres under Non-Plane Wave Illumination," SPIE Int'l Symp. on Lasers, Sensors, and Applications (OE LASE '93), Los Angeles, CA, January 20, 1993.
- Hodges, J.T., "Elastic Scattering from Spheres under Non-Plane Wave Illumination," Scientific Conf. on Obscuration and Aerosol Research, Edgewood Research, Development and Engineering Center, Dept. of the Army, Edgewood, MD, June 22, 1993.
- Houser, J.F., "NIST/API Update for the Improvement of Uncertainties for Volumetric Test Measures," API CODM, Dallas, TX, March 24, 1993. Invited
- Huang, P.H., "Thermodynamic Properties of Moist Air Containing 1000 to 5000 PPMv of Water Vapor," RL/NIST Workshop on Moisture Measurement and Control for Microelectronics, April 5, 1993.
- Huang, P.H., "Humidity Measurement and Standards," ASME International Solar Energy Conference, April 26, 1993. Invited
- Hurst, W.S., "NIST Optically Accessible SCW Reactor Flow Cell," International Workshop on Supercritical Water and Fluid Chemistry - Waste Treatment and Future Chemical Processes, Kernforschungszentrum, Karlsruhe, Germany, March 26, 1993.
- Kreider, K.G., "Sputtered High Temperature Thin Film Thermocouples," American Vacuum Society 39th National Symposium, Chicago, IL, November 11, 1992.
- Kreider, K.G., "Thin Film High Temperature Silicide Thermocouples," ISA, 39th International Instrumentation Symposium, Albuquerque, NM, May 5, 1993. Invited
- Mangum, B.W., "The Thermometry Program at the National Institute of Standards and Technology," ISA Meeting, Bethesda, MD, June 2, 1993. Invited
- Mattingly, G.E., "Fluid Flowrate Metrology - National Standards and Traceability," International Symposium on Metrology, Centro Nacional De Metrologia, Mexico City, Mexico, October 6, 1992. Invited
- Mattingly, G.E., "Flow Measurement - Calibration Techniques and Installation Effects," NCSL Region 3, Johns Hopkins Applied Physics Laboratory, Columbia, MD, October 21, 1992. Invited
- Mattingly, G.E., "Flow Measurement Traceability Using Round Robin Techniques," NIST Office of Weights and Measures Workshop, Annapolis, MD, October 22, 1992. Invited

- Mattingly, G.E., "Flow Measurement Programs at NIST, An Update," ASME Fluid Metering Committee Meeting, Orlando, FL, November 5, 1992. Invited
- Mattingly, G.E., "Progress Review on Installations Effects Research," NIST Consortium Meeting, Gaithersburg, MD, November 10, 1992.
- Mattingly, G.E., "Flowmeter Installation Effects Research at NIST and SWRI - The Tee Used as an Elbow," International Gas Research Conference Meeting, Orlando, FL, November 18, 1992.
- Mattingly, G.E., "Round Robin Gas Flow Measurement," SEMATECH, Austin, TX, January 25, 1993.
- Mattingly, G.E., "Flowmeter Installation Effects: The 45° Elbow," AGA Gas Metering Research Council/Southwest Research Institute Technical Advisory Committee Meeting, San Antonio, TX, January 26, 1993. Invited
- Mattingly, G.E., "Prospects for Future Research in Flowmeter Installation Effects," Southwest Research Institute/Gas Research Institute/Technical Advisory Committee Meeting, Upstream Effects Sub. Committee, San Antonio, TX, January 28, 1993.
- Mattingly, G.E., "Gas Flow Measurement: Calibrations, Standards, and Traceabilities," NCSL Region 7, Quarterly Meeting, Santa Clara, CA, February 11, 1993. Invited
- Mattingly, G.E., "Flowmeter Installation Effects," NCSL Region 7, Quarterly Meeting, Santa Clara, CA, February 11, 1993. Invited
- Mattingly, G.E., "Gas Flow Measurement Using Surrogate Fluid Theories," NCSL Region 7, Quarterly Meeting, Santa Clara, CA, February 11, 1993. Invited
- Mattingly, G.E., "Proposed Improvements in NIST's Liquid Volume Measurement Services to Meet API Requests," Committee on Petroleum Measurements Meeting, NIST, Gaithersburg, MD, February 16, 1993.
- Mattingly, G.E., "NIST Flowmeter Installation Effects Research Topics for GRI Support in 1993," Gas Research Institute, February 26, 1993.
- Mattingly, G.E., "NIST-SEMATECH Round Robin Gas Flow Measurement Program," OTA Review, NIST, Gaithersburg, MD, March 16, 1993. Invited
- Mattingly, G.E., "CFD Results for the Liquid-Only Flow in Selected Atomizer Geometries," SiGMA Consortium Meeting, NIST Materials Building, March 31, 1993.

- Mattingly, G.E., "NIST Calibration Services for Airspeed Measurement," EPRI Continuous Emission Monitoring (CEM) Conference, Baltimore, MD, April 14, 1993. Invited
- Mattingly, G.E., "Flow Measurement," Short-Course presented at the 39th ISA International Instrumentation Symposium, Albuquerque, NM, May 3, 1993. Invited
- Mattingly, G.E., "Flowmeter Installation Effects on Orifice Meters," AGA Distribution/Transmission Conference, Orlando, FL, May 17, 1993.
- Mattingly, G.E., "Flowmeter Installation Effects: Wild Claims, Bright Ideas, and Stark Realities," ASME Fluid Measurement Symposium, Washington, DC, June 29, 1993.
- Mattingly, G.E., "Flow Measurement," Short Course presented at CENAM, Mexico City, Mexico, September 27-28, 1993. Invited
- Meyer, C.W., "Realizations of the Triple Points of Argon, Oxygen and Neon for the NIST Realization of the ITS-90," Spring Meeting of the American Physical Society, Washington, DC, April 12, 1993.
- Meyer, C.W., "Measurements of the Gas Dependence of the Effective Area of a Piston Gage Using H<sub>2</sub>, <sup>3</sup>He, <sup>4</sup>He, N<sub>2</sub>, CO<sub>2</sub>, and SF<sub>6</sub>," CCM Second Seminar on "Pressure Metrology from 1 kPa to 1 GPa", Paris, France, June 2, 1993. Invited
- Poirier, G.E., "The Growth and Manipulation of Ultra-Thin Rhodium Films on TiO<sub>2</sub>(001) Characterized by Scanning Tunneling Microscopy and Auger Electron Spectroscopy," American Vacuum Society 39th National Symposium, Chicago, IL, November 10, 1992.
- Poirier, G.E., "Properties of Ultrathin Heteroepitaxial SnO<sub>2</sub> Films," American Vacuum Society 39th National Symposium, Chicago, IL, November 11, 1992.
- Poirier, G.E., "Characterization of Oxide-Supported Metal Particles by Tunneling Microscopy," Exxon Research and Engineering, Annandale, NJ, April 13, 1993. Invited
- Presser, C., "Observations of Soot in Combustion of Methanol/Toluene Spray Flames," 1992 ASME Winter Annual Meeting, Anaheim, CA, Nov. 9, 1992.
- Presser, C., "Behavior of Droplets in Pressure-Atomized Fuel Sprays," 31st AIAA Aerospace Sciences Meeting, Reno, NV, January 11, 1993.
- Presser, C., "Time-Based Analysis of Phase/Doppler Data," SPIE Int'l Symp. on Lasers, Sensors, and Applications (OE LASE '93), Los Angeles, CA, January 19, 1993.



- Presser, C., "Influence of Mixture Composition on Soot Formation in Methanol/Toluene Spray Flames," Joint Technical Meeting, Central and Eastern States Sections of the Combustion Institute, 527-531, New Orleans, LA, March 17, 1993.
- Presser, C., "Droplet Transport in Nonswirling Pressure-Atomized Fuel Sprays Using Phase Doppler Interferometry," 6th Annual Conf. on Liquid Atomization and Spray Systems (ILASS Americas '93), Worcester, MA, May 17, 1993.
- Presser, C., "Effect of Finite Beam Width on Elastic Light Scattering From Droplets," 6th Annual Conf. on Liquid Atomization and Spray Systems (ILASS Americas '93), Worcester, MA, May 18, 1993.
- Presser, C., "Effect of Finite Beam Width on Elastic Light Scattering From Droplets," Gordon Research Conf. on the Physics and Chemistry of Laser Diagnostics in Combustion, July 12, 1993.
- Presser, C., "Behavior of Droplets in Pressure-Atomized Fuel Sprays with Coflowing Air Swirl," ASME National Heat Transfer Conf., Atlanta, GA, August 9, 1993.
- Radebaugh, R., "Graded and Nongraded Regenerator Performance," 7th International Cryocooler Conference, Santa Fe, NM, November 18, 1992.
- Radebaugh, R., "Design Equations and Scaling Laws for Linear Compressors with Flexure Springs," 7th International Cryocooler Conference, Santa Fe, NM, November 18, 1992.
- Ripple, D., "Dynamic Contact Angle of a Liquid Spreading on a Heated Plate," American Physical Society Meeting, Washington, DC, April 14, 1993.
- Rosasco, G.J., "Research and Measurement Services of Potential Interest to the NASA Metrology and Calibration Working Group," 16th Annual NASA Metrology and Calibration Workshop, April 2, 1993.
- Scott, J.L., "Results of GRI-Funded Research with the Two-inch Orifice Meter in Nitrogen Gas," NIST Industry-Government Consortium on Flowmeter Installation Effects, Gaithersburg, MD, November 10, 1992.
- Scott, J.L., "Results of GRI-Funded Orifice Meter Research at NIST Boulder," AGA Gas Metering Research Council/Southwest Research Institute Technical Advisory Committee Meeting, San Antonio, TX, January 27, 1993.
- Scott, J.L., "Comparing NIST-B 50 mm Orifice Meter Gas Data to the ANSI Equation," Forum on Fluid Measurement and Instrumentation, ASME Fluids Engineering Division Summer Meeting, Washington, DC, June 21, 1993.

- Scott, J.L. for Radebaugh, R., "The Measurement of Oscillating Mass Flows at Low Temperatures," Symposium on Devices for Flow Measurement and Control, ASME Fluid Engineering Division Summer Meeting, Washington, DC, June 23, 1993. Invited
- Semancik, S., "The Use of Surface and Thin Film Science in the Development of Advanced Gas Sensors," 12th International Vacuum Congress and 8th International Conference on Solid Surfaces, The Hague, The Netherlands, October 15, 1992. Invited
- Semancik, S., "Surface, Interface and Thin Film Studies Related to Chemical Sensing," Linkoping Institute of Technology, Linkoping, Sweden, October 19, 1992. Invited
- Semancik, S., "Surface and Materials Research in the Development of Oxide-Based Gas and Solution Sensors," Department of Electrical Engineering, University of Twente, Enschede, The Netherlands, October 22, 1992. Invited
- Semancik, S., "Properties of Surface-Modified SnO<sub>2</sub> and IrO<sub>2</sub>," 39th National Symposium of the American Vacuum Society, Chicago, IL, November 9, 1993.
- Semancik, S., "Catalytic Aspects of Gas Microsensor Arrays," Gordon Conference on Catalysis, New London, NH, June 29, 1993.
- Semancik, S., "NIST Facilities and Programs in Gas Sensing", NIST Workshop on Gas Sensors, Gaithersburg, MD., September 8, 1993.
- Sobolewski, M.A., "Measuring the Distribution of Current in the G.E.C. Reference Cell," 45th Annual Gaseous Electronics Conference, October 27, 1992.
- Sobolewski, M.A., Djurovic, S., Olthoff, J.K., Roberts, J.R., and Whetstone, J.R., "Measuring the Distribution of Current in rf Glow Discharges," American Vacuum Society 39th National Symposium, November 9, 1992.
- Sobolewski, M.A., "Electrical Sensors for Monitoring RF Plasma Sheaths," Microelectronic Processing 92, SPIE, Monterey, CA, September 29, 1993.
- Strouse, G.F., "NIST Measurement Assurance of SPRT Calibrations on the ITS-90: A Quantitative Approach," 1993 Measurement Science Conference, Anaheim, CA, January 21, 1993. Invited
- Tarlov, M.J., "Ultraviolet Photoelectron Spectroscopy of Alkanethiol Monolayers Self-Assembled on Gold," 39th National Symposium of the American Vacuum Society, Chicago, IL, November 13, 1992.

- Tarlov, M.J., "Photopatterning of Alkylthiol Self-Assembled Monolayers," 205th American Chemical Society National Meeting, Denver, CO, March 20, 1993. Invited
- Tew, W.L., "Anelastic Loss in BeCu Torsion Fibers," American Physical Society Meeting, Washington, DC, April 12, 1993.
- Tew, W.L., "New Procedures and Capabilities for the Calibration of Cryogenic Resistance Thermometers at NIST," Cryogenic Engineering Conference, Albuquerque, NM, July 13, 1993.
- Yeh, T.T., "Flowmeter Installation Effects, 45° Elbow," NIST Industry-Government Consortium on Flowmeter Installation Effects, Gaithersburg, MD, November 10, 1992.
- Yeh, T.T., "Flowmeter Installation Effect," Southwest Research Institute/Gas Research Institute/Technical Advisory Committee Meeting, Upstream Effects Sub. Committee, San Antonio, TX, January 27, 1993. Invited
- Yeh, T.T., "Pipeflow Downstream of a Reducer and its Effects on Flowmeters," ASME Fluids Engineering Conference, Washington, DC, June 21, 1993.
- Zachariah, M.R., "Ab-Initio Studies of Important Silicon-oxygen Reactions," AIChE Symposium on Gas Phase Kinetics in Electronic Materials Processing, Miami Beach, FL, November 2, 1992.
- Zachariah, M.R., "Principles of Vapor Phase Formation of Ceramic Particles During Combustion," Particle Technology Center, Penn State University, PA, February 8, 1993. Invited
- Zachariah, M.R., "Principles of Vapor Phase Formation of Ceramic Particles During Combustion," Physical Chemistry/Chemical Physics Seminar Series, University of Maryland, College Park, MD, April 21, 1993. Invited
- Zachariah, M.R., "Chemical Principles of Vapor Phase Formation of Ceramics," Yale University, Dept. of Mechanical Engineering, New Haven, CT, May 5, 1993. Invited

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

Reactions in Near-Critical Water, Gregory J. Rosasco  
CONOCO Inc. (CRADA)

Processing of Ceramic Powders, Michael R. Zachariah  
NanoPhase Technologies (CRADA)

Chemical Measurements for Power Plants, Wilbur Hurst  
Babcock & Wilcox Company (CRADA)

Filter Materials Accelerated Life Testing, S. Rao Charagundla and A. Maček  
Pall Corporation (CRADA)

On-line Spectroscopy of Various Metalorganics used in Compound Semi Conductors, S. Rao  
Charagundla  
Morton International/CVD Metalorganics (CRADA)

Thermal Processes and Hazardous Waste Destruction, Cary Presser and Joseph T. Hodges  
Scientific Applications International Corporation (CRADA)

Combustion of Acoustically Driven Atomized Sprays, Cary Presser  
Fluid Jet Associates (CRADA)

Development of 400 Hz OPTR, Ray Radebaugh  
Tektronix (CRADA) (pending)

Liquid Piston Heat Engine, Ray Radebaugh  
Clovis Thermal (CRADA)

Pulse Tube Refrigerator Test Facility, Ray Radebaugh  
Hughes Aircraft (CRADA)

Flowmeter Installation Effects Consortium, George 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  
Ford Motor Company  
Gas Research Institute  
Institute of Paper Science and Technology  
Instrument Testing Services  
Ketema - McCrometer Division  
Ketema - Schutte & Koerting Division  
Kimmon Manufacturing Company, Ltd. (Japan)  
N.V. Nederlands Gasunie  
NOVA Husky Research Center  
Pacific Gas & Electric Company  
Rosemount, Inc.

Supersonic Inert-Gas Metal Atomization Consortium, George E. Mattingly  
Ampal/Metallurgy  
Crucible Materials Co.  
DoE/Office of Industrial Processes  
General Electric Aircraft Engines  
Martin Marietta  
United Technologies - Pratt & Whitney

#### 4. Patent Awards and Applications

Kreider, K.G., "Metal Silicide Thin Film Thermocouples" (Submitted June 1993)

Kreider, K.G., "Method for Bonding Thin-Film Thermocouples to Ceramics," Patent No. 5,215,597 (Issued June 1993)

Poirier, G.E., "Atomic Force Microscope Using Piezoelectric Detection" (Submitted September 1993)

Siegwarth, J.D., "Energy Efficient Pumping of Liquids into High Pressure Reactors and the Application of the Technique to Aqueous Supercritical Oxidation" (Submitted February 1993)

Tarlov, M.J., "UV-Photopatterning of Alkylthiolate Monolayers Self-Assembled on Gold and Silver" (Submitted April 1993)

#### 5. SRM Activities

SRM 1972 Ethylene Carbonate Triple-Point Temperature Standard (completed)

SRM 1973 n-Docosane Triple-Point Temperature Standard (completed)

SRM 1746 Silver Freezing-Point Standard (completed)

SRM 1744 Aluminum Freezing-Point Standard (in progress)

#### 6. SRD Activities

A cooperative effort between the Fluid Systems Group and Standard Reference Data has resulted in an Orifice Meter Database Product to be released early in FY94.

## 7. Calibrations

Calibration services have been provided for the following:

Accuracy Scientific Inst.	Certified Measurement Services
Aerospace Optics Inc.	CGS Thermodynamics
Air Force Newark	CI Systems
Air Products & Chemicals Inc.	Climatronics Corp.
Airflow Technical Products Inc.	Commonwealth Edison Co.
Alcan-Toyo America	Commonwealth of Massachusetts
Alden Research Lab Inc.	Comtel Instruments Co.
Allegheny Power System	Conax Buffalo Corp.
Allied Signal Inc.	Conrad Kacsik Inst Sys Inc.
Alnor Instrument Co.	Consumers Power Co.
Aluminum Co of America	Control Co.
American Electro Products Inc.	Convectronics Inc.
Amegen Inc.	Corning Inc.
Amoco Oil	Cosa Instrument Co.
Amphenol	Cozad Instrument Co.
Amsco	Cytem Specialty Steel
Analog Devices	Detroit Edison
Arizona Public Service Co.	Douglas Aircraft Co.
Arnold AFS	DRB Industries
AT&T	DuPont Pharmaceuticals Inc.
Auto Paint Center	Duke Power Co.
Automatic Systems Labs Inc.	Duro Sense Corp.
AVX Corp.	E-Systems Inc.
Babcock & Wilcox	Eastern Stainless Corp.
Baltimore Aircoil Co.	Eastman Kodak Co.
Baltimore Gas & Electric Co.	Eaton Ail Systems Inc.
Battelle Memorial Institute	EG&G Idaho Inc.
Becton Dickinson & Co.	EG&G Inc.
Belfort Instruments	EG&G Rocky Flats Inc.
Bell Helicopter Textron Inc.	EG&G Rotron Inc.
BHP Petroleum America Refining	EI Dupont De Nemours & Co. Inc.
Boonton Electronics Corp.	Engelhard Corp.
Brooklyn Thermometer Co Inc.	Engelhard West Inc.
Brooks Instruments	Engineering Measurement Co.
Buckeye Pipe Line Co.	Enseco Wadsworth Alert Labs
C-Temp	Environmental Systems Corp.
California Alloy Co.	ETL Testing Labs Inc.
Carpenter Technology Corp.	Ever Ready Thermometer Co Inc.
CGS Thermodynamics	Exxon Co USA

Fenwal Electronics Inc.  
Fisher Scientific Co.  
Flowdata Inc.  
Francis Freas Glass Works Inc.  
Furnace Parts Inc.  
Gay Engineering & Sales Co Inc.  
GE Aircraft Engines  
GE Astro Space  
GEC Marconi Electronic Systems  
Geltech Inc.  
General Dynamics  
General Eastern Instruments  
General Motors Corp.  
Gibraltar Biological Labs Inc.  
Gossman Instrument Svc.  
Grumman Aerospace Corp.  
GTE/ERS  
Guildline Instruments Inc.  
Halliburton Nus Corp.  
Hanna Instruments Inc.  
Hanna Instruments of America  
HB Instrument Co.  
Hoechst Celanese  
Hoffer Flow Controls Inc.  
Holometrix  
Honeywell Inc.  
Hoskins Mfg. Co.  
Howmet Corp.  
Humana Hospital Northside  
Huntsman Chemical Corp.  
Hutchinson Technology  
Industronics Service Co.  
Inspectorate  
Instrulab Inc.  
Instrument Lab.  
Intech Automation Sys Corp.  
J & W Scientific  
John Fluke Mfg. Co. Inc.  
Johnson Controls World Svcs.  
Johnson Matthey  
Joliet Metallurgical Labs Inc.  
Jorgensen Forge  
Kaman Aerospace Corp.

Kaye Instruments Inc.  
Kayness Inc.  
Keithley Instruments Inc.  
Kessler Instruments Inc.  
Klock  
Kurz Instruments Inc.  
Lee Co.  
Lockheed Abilene Facility  
Lockheed Eng. & Sciences Co.  
Lockheed Missiles & Space Co.  
Luxtron Corp.  
Magnavox Electronic Systems  
Magnavox Electronic Systems Co.  
Mapco Inc.  
Marlin Mfg. Corp.  
Martin Marietta Astronautics  
Martin Marietta Corp.  
Martin Marietta Energy Sys.  
Martin Marietta Specialty  
Massachusetts Inst of Tech.  
McDonnell Douglas Aircraft Co.  
McDonnell Douglas Corp.  
McGill Mfg. Co. Inc.  
MD Instruments Inc.  
Medtherm Corp.  
Melcam Standards Lab  
Metcut Research Associates Inc.  
Meter Check Inc.  
Meter Engineers Inc.  
Mid America Pipeline Co.  
Miles Inc.  
Miller & Weber Inc.  
Mocon Modern Controls Inc.  
Modern Instrument Co. Inc.  
Montgomery County Gov't  
Moore Special Tool Co. Inc.  
Morehouse Instrument Co.  
MDP Inc.  
MSE Inc.  
NASA Langley Research Ctr  
National Weather Service  
Nature Form Inc.  
Naval Weapons Station

Navy Primary Stds Lab West  
Nelson Instrument Svc Co Inc.  
Nelson Jameson Inc.  
Northwest Research Assoc Inc.  
Nutrasweet Co.  
NYS College of Ceramics  
Omega Engineering Inc.  
Ontario Hydro Service Centre  
Ortho Pharmaceutical Corp.  
PA Power & Light Co.  
Pacific Gas & Electric Co.  
Paramax Systems Corp.  
Parameter Generation & Control  
Parker Hannifin Corp.  
Pemberton Fabricators Inc.  
Pemco Aeroplex Inc.  
Philadelphia Electric Co.  
Philips Lighting Co.  
PMC Corp.  
PPG Industries  
Pratt & Whitney  
Process Instruments Inc.  
Projects Inc.  
Pyco Inc.  
PSE&G Co.  
Pyromation Inc.  
Pyrometric Service Co  
Qualimetrics Inc.  
R P Services  
Rainwise Inc.  
Raytheon Co.  
Respiratory Support Prod Inc.  
Reynolds Electrical & Eng. Co.  
RM Young Co.  
Rockwell International  
Rosemount Inc.  
Sandia National Labs  
Sanofi Diagnostics Pasteur Inc.  
Santa Barbara Infrared Inc.  
SC Electric & Gas Co.  
Seminole Pipeline Co.  
Sensing Devices Inc.  
Service Associated Inc.

SGS-Thomson Microelectronics  
Shell Oil Co.  
Sherwood Medical  
Sherwood Medical Co.  
Signetics Co.  
Simco Electronics  
Simmonds Precision Products  
SISIR  
Smith Meter Inc.  
Smith Systems  
Solomat/Neotronics Co.  
South Riding Point Holding  
Southern CA Edison Co.  
Special Metals Corp.  
Spectrodyne Inc.  
Sper Scientific Ltd.  
St. Jude Medical Inc.  
Standard Thomson Corp.  
State of California  
State of Hawaii  
State of New York  
Stillins Instrument Systems  
Teledyne Geotech  
Teledyne Systems Co.  
Tennessee Valley Authority  
Teradyne Inc.  
Texas Instruments  
Thermo Electric Co. Inc.  
Thermogage Inc.  
Thermometrics  
Thompson Equipment Co.  
Tobacco Inst. Testing Lab  
Toledo Edison Co.  
Trans Traders Corp.  
Transmation Inc.  
TRW Space & Defense Sector  
TSI Inc.  
TU Electric  
Tudor Technology Inc.  
Unified Industries Inc.  
Unisys Corp.  
US Army TMDE Activity  
US Customs Service



US Dept. of the Interior  
Vaisala Inc.  
Valley Heat Treat Co.  
W L Walker Co. Inc.  
Watlow Gordon  
Weed Instrument  
Westinghouse Electric Corp.  
Westinghouse Savannah River Co.  
Wright Patterson Air Force  
Wyeth Ayerst Labs  
York International Corp.  
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-20.94, Publications  
Instrument Society of American SP-1.1, Committee on Temperature Measurement  
(Thermocouples)

### **W.G. Cleveland**

CSTL Safety Committee

### **R.R. Fink**

NIST Metals Storeroom Commodities Meetings

### **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

### **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. Maček**

Combustion Institute - 25th Symposium (International) on Combustion, Program Subcommittee  
AIChE Area 3B Committee on Fluidization and Fluid Particle Systems  
CSTL Strategic Planning Committee on Environment (Chair)

#### **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

#### **B.W. Mangum**

ASTM E-20 Committee on Temperature Measurement  
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  
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)

**E. Marquardt**

Boulder Editorial Review Board Member

**D.A. Olson**

Boulder Editorial Review Board

CSTL Colloquium Committee Member

**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 Nat'l Energy Terrestrial Systems Technical Committee

ASME International Joint Power Generation Conference, Modeling of Combustion Systems (Co-chairman)

ASME Winter Annual Meeting, Heat Transfer in Hazardous Waste Processing (Co-chairman)

6th Annual Conf. on Liquid Atomization and Spray Systems, Atomization Processes (ILASS Americas '93) (Co-chairman)

ASME National Heat Transfer Conf., Fire and Combustion Systems - Droplets and Sprays, and Fire and Combustion Systems - Industrial Combustion Systems I and II (Co-chairman)

International Joint Power Generation Conf., Modeling of Combustion Systems (Co-chairman)

ASME Winter Annual Meeting, Symposium on Fluid Mechanics and Heat Transfer in Sprays, Heat and Mass Transfer in Spray Combustion Systems (Co-chairman)

CSTL Strategic Planning Committee on Energy Technology

**R. Radebaugh**

7th International Cryocooler Conference Advisory Committee

8th International Cryocooler Conference Local Arrangements (Chairman)

**M.L. Reilly**

ASTM E-20 Committee on Temperature Measurement

ASTM Subcommittee E-20.02, Radiation Thermometry Working Group E-20.02.01, Test Methods (Chairman)

ASTM Subcommittee E-20.06, New Thermometers and Techniques

ASTM Subcommittee E-20.07, Fundamentals in Thermometry

ASTM Subcommittee E-20.91, Editorial and Nomenclature

**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  
CSTL Strategic Planning Committee on Chemical Process Technology

**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

**M.G. Scroger**

ASTM E-20 Committee on Temperature Measurement  
ASTM E-20.04, Thermocouples  
ASTM E-20.06 New Thermometers and Techniques

**S. Semancik**

American Vacuum Society, Thin Film Division, Program Committee  
NIST Workshop on Gas Sensors: Strategies for Future Technologies, Organizing  
Committee (Chairman)  
CSTL Colloquium Committee Member

**G.F. Strouse**

CSTL Electronic Notebook Policy Committee

**M.J. Tarlov**

CSTL Strategic Planning Committee on Biotechnology (Member)

**J.R. Whetstone**

ISA Standards and Practices, Board of Directors  
CSTL Strategic Planning Committee on Electronics (Chair)  
Semiconductor Industries Roadmap Planning Workshop, Equipment Modeling and  
Design Working Group

**J.A. Wise**

ASTM E-20 Committee on Temperature Measurement (Chairman)  
ASTM Subcommittee E-20.05, Liquid-in-Glass Thermometers and Hydrometers  
(Secretary)  
ASTM Subcommittee E-20.90, Executive Subcommittee (Chairman)  
ASTM Subcommittee E-20.91, Editorial and Nomenclature (Secretary)

**M.R. Zachariah**

Combustion Institute - 25th Symposium (International) on Combustion, Program Subcommittee

AAAR Aerosol Technology Group (Chairman)

AICHE Material Engineering & Science, Aren 8d. - Ceramics

NIST Focus Group on Industrial Application of Computational Chemistry

NIST/SEMATECH Chemical Kinetics Data Base Steering Committee

CSTL Strategic Planning Committee on Advanced Materials

**9. Editorships**

**G.E. Mattingly**

International Journal of Flow Measurement and Instrumentation (North American Editor)

**C. Presser**

Proc. Heat Transfer in Fire and Combustion Systems, HTD-Vol. 250, 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, 1992**

Cary Miller, University of Maryland, College Park, MD, "Measuring Electron Transfer Reactivity at Insulated Electrodes: A Start to Molecular Electronic Devices." (Division Sponsor: M.J. Tarlov)

**December 11, 1992**

Harry W. Sarkas, Johns Hopkins University, Baltimore, MD, "The Generation of Nanometer Dimensional Clusters and Cluster Ions via Inert Gas Condensation." (Division Sponsor: M.R. Zachariah)

**February 3, 1993**

Dr. Ulrike Diebold, Rutgers, The State University of New Jersey, Piscataway, NJ, "Ultrathin Metal Films on TiO<sub>2</sub>(110): Growth, Structure and Surface Reactivity." (Division Sponsor: S. Semancik)

**February 24, 1993**

Dr. Valeriy Sukharev, Karpov Institute of Physical Chemistry, Moscow, "Physics and Chemistry of Adsorption-Induces Response of Electrical characteristics of Semiconductor Adsorbents." (Division Sponsor: S. Semancik)

**March 17, 1993**

C.L. Marshall, Amoco Oil Company, Research & Development Department, Naperville, IL, "Molecular Modeling of Catalysts and Catalytic Surfaces." (Division Sponsor: P. Westmoreland)

**March 26, 1993**

Dr. Tyler B. Thompson, The Dow Chemical Company, Midland, MI, "Application of Gas-Phase Kinetic Models in The Dow Chemical Company." (Division Sponsor: P. Westmoreland)

**March 28, 1993**

Brian McMillin, Stanford University, Stanford, CT, "Instantaneous Two-Line PLIF Temperature Imaging of Nitric Oxide in Supersonic Mixing and Combustion Flowfields." (Division Sponsor: M. Zachariah)

**April 28, 1993**

A.W. Marshall, University of Maryland, College Park, MD, "Incipient Buoyant Convective Criticality In a Differentially Heated Horizontal Cylinder." (Division Sponsor: P.I. Espina)

**May 6, 1993**

Suhas V. Patankar, University of Minnesota, Minneapolis, MN, "Some Numerical Studies of Fluid Flow and Heat Transfer Problems." (Division Sponsor: G.E. Mattingly)

**May 21, 1993**

Max M. Tirtowidjojo, The Dow Chemical Company, Midland, MI, "Fundamental Kinetic Modeling for Industrial Reactors." (Division Sponsor: P. Westmoreland)

**June 23, 1993**

Richard B. Hall, Exxon Research and Engineering, Annandale, NJ, "Kinetics and Mechanisms of Methyl Reactions on Ni(100) and NiO(100) Surfaces." (Division Sponsor: G.E. Poirier)

**June 24, 1993**

James J. Hickman, Science Applications International Corporation, McLean, VA, "The Use of Monolayers as Templates for in vitro Cellular Networks." (Division Sponsor: M.J. Tarlov)

**June 25, 1993**

R.A. Dobbins, Brown University, Providence, RI, "Precursor Particles in Hydrocarbon Flames." (Division Sponsor: M.R. Zachariah)

**August 17, 1993**

Charles L. Merkle, Penn State University, State College, PA, "The Role of Physics in the Convergence of CFD Algorithms." (Division Sponsor: G.E. Mattingly)

**August 18, 1993**

Burt V. Bronk, Edgewood Research Development and Engineering Center, Aberdeen, MD, "Optical Interrogation of Single Biological Particles." (Division Sponsor: J.T. Hodges)

**September 8, 1993**

Sivarem P. Gogineni, Florida State University, Tallahassee, FL, "An Overview of Particle Image Velocimetry (PIV)." (Division Sponsor: G.E. Mattingly)

**September 28, 1993**

Thomas J. McAvoy, University of Maryland, College Park, MD, "Using Neural Networks to Improve Process Operation and Control." (Division Sponsor: D.A. Olson)

**11. Conferences/Workshops/Sessions Sponsored/co-Sponsored**

**October 13-16, 1992**

Materials Processing Session, American Association for Aerosol Research (AAAR) 1992 Annual Meeting, San Francisco, CA (M.R. Zachariah)

**November 2, 1992**

High Temperature Processing of Materials Session, American Institute of Chemical Engineers (AIChE) 1992 Annual Meeting, Miami Beach, FL (M.R. Zachariah)

**November 2-6, 1992**

Precision Thermometry Workshop, National Institute of Standards and Technology, Gaithersburg, MD (B.W. Mangum)

**November 10, 1992**

Flow Meter Installation Effect Consortium Meeting, NIST-Gaithersburg, MD (G.E. Mattingly and T.T. Yeh)

**March 15-19, 1993**

Precision Thermometry Workshop, National Institute of Standards and Technology, Gaithersburg, MD (B.W. Mangum)

**April 15, 1993**

Workshop on Waste Processing and Minimization, National Institute of Standards and Technology, Gaithersburg, MD (A. Maček)

**May 19-20, 1993**

NIST Workshop on Industrial Applications of Computational Chemistry, Gaithersburg, MD (M.R. Zachariah)

**May 25-27, 1993**

Workshop on Computational Fluid Dynamics of Supersonic Inert Gas Metal Atomization (SiGMA) Flows, Gaithersburg, MD (P.I. Espina)

**September 9-10, 1993**

NIST Workshop on Gas Sensors: Strategies for Future Technologies, Gaithersburg, MD (S. Semancik)

**September 15-16, 1993**

Workshop on Identification of Critical Measurement Needs for Waste Minimization from Industrial Processes, National Institute of Standards and Technology, Gaithersburg, MD (A. Lee)



## VI. Surface and Microanalysis Science Division (937)

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 as well as source apportionment in atmospheric chemistry, and (e) develop and certify Standard Reference Materials and Standard Reference Data. In these broad based efforts, 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, at interfaces, and in microstructures. This information is needed to understand the relationships between processing results, devices, or material properties and chemical composition in various technologies, such as chemical catalysis, advanced electronics, and materials science. This understanding provides the basis to develop new processes for bulk or specialty chemicals, advanced alloys, and surface-modified, magnetic, and electronic materials.

Measurement Science - Technique Extension and Development. A significant part of our research in measurement science involves the development of new techniques and the application of state-of-the-art techniques to characterize chemical systems. We also apply the results of our research to areas of national priorities for Other Government Agencies, various industries, academia, and other laboratories in NIST. Some recent accomplishments follow.

Using a new ultrafast femtosecond laser system and second order non-linear optics, we have developed and used a sum-frequency generation and measurement technique to characterize thin Si layers ( $\sim 20$  nm) on  $\text{CoSi}_2$  films, producing a unique signal from Si/ $\text{CoSi}_2$  interfaces from which we can identify symmetry and twinned and untwinned surfaces. This non-destructive measurement technique shows promise for the *in situ* monitoring of thin-film deposition processes. We have also used ultrashallow secondary ion mass spectrometry (SIMS) and grazing-incidence-angle x-ray photoelectron spectroscopy to identify oxides (and other species) within 100 nm and 10 nm, respectively, of surfaces. This combination of techniques provides information that will be invaluable in determining surface layers on various types of materials.

In collaboration with NIH, our breakthrough success in establishing trace nanoanalysis as a viable, applicable technique that provides us with the capability to characterize materials from

major, minor, to trace chemical concentrations at nanometer spatial scales has been reported in *Analytical Chemistry*. This technique continues to be applied to practical problems in electronics, materials, and coatings. It will be useful to industry for determining trace contaminants, phase and chemical homogeneity in starting or end products, as well as assessing manufacturing steps and their impact on the chemical composition at high spatial resolution.

Particle sampling and analysis, including characterization of environmentally hazardous individual particles and populations of particles from various sources, constitute a significant effort within the Division. Studies with automated scanning electron microscopy (SEM) to characterize particle populations have shown that normalization of results for particle size and use of conventional ZAF/bulk standards correction procedures provides adequate accuracy for most particle measurements. We continue our efforts in electron probe research which include micro-area x-ray fluorescence and applications (compositional mapping of industrially-produced high- $T_c$  superconductors with Biomagnetic Technologies), and extensive efforts for particle analyses for other Government Agencies. We determined the accuracy of first-principle x-ray spectrum simulation with Desktop Spectrum Analyzer (DTSA), a comprehensive x-ray spectrum simulation and deconvolution calculation "engine" with an associated x-ray database. We received a patent for DTSA, the first patent issued for a combination software and database at NIST. DTSA, offered for sale through the Office of Standard Reference Data, has sold almost 125 copies.

In microprobe techniques, we continued our efforts to increase sensitivity and spatial resolution of analyses. In SIMS, we: 1) developed imaging of self-assembled monolayers (SAMs, with M. Tarlov, Division 836) and investigated other procedures using electron and ion bombardment to produce SAMs with different chemical species and patterns; 2) evaluated silicon wafer cleaning procedures (with the Naval Research Laboratory); and 3) developed high spatial resolution isotope ratio imaging and applied it to variations in samples such as the Allende meteorite. We also are developing the capability for elemental and isotopic characterization of submicrometer spatial areas using TOF-SIMS, and are developing the capability to measure therapeutic drug and metal localizations in human tissue (with NIH) and drugs-of-abuse localization in tissue and hair (with NIH and Division 835). A new type of ion-induced surface reaction mechanism was identified in inorganic compounds by the systematic analysis of certain ion-excited Auger-electron features that are dependent on relevant electron levels in different compounds. The mechanism is believed to be important in the modelling of ion-surface interactions, in ion-promoted surface modifications, and in the long-term stability of nuclear waste storage materials.

In spatially resolved and particle measurements, we used the video radiation detector to locate alpha particle emitters from specific actinides in reference materials, minerals, and environmental samples. We completed our collaboration with the Army, which included studies on mass transport and aerosol flow to aid in the leak testing of gas masks. In continued collaboration with the National Fluid Power Association to produce a Particles-in-Oil SRM, we made initial measurements on a prototype material. This SRM, critical for international

measurement standardization, will be used to determine particle contamination in power transfer fluids. We also developed a CRADA with HiAc/RoyCo for some of these measurements.

In our Congressionally mandated asbestos programs, our emphasis has been in technology transfer. In the program for analyzing bulk asbestos in building materials, we have worked closely with NVLAP (NIST), EPA, and commercial laboratories. We had the major responsibility for all technical aspects of measurement accuracy, SRM development and certification, method development for characterizing proficiency test materials, and accreditation of the more than 800 laboratories since the program's inception. During the past year, we successfully transferred this major responsibility to industry and are maintaining an oversight role for quality assurance (QA). In the airborne asbestos program (again in close collaboration with more than 100 testing laboratories, EPA, and NVLAP), we attained quality analysis of airborne asbestos through a rigorous proficiency testing, standards, and methods research program. We are transferring these efforts to industry while we maintain a QA role (as done for bulk asbestos).

Also in the environmental arena, we continue our major programs in the areas of atmospheric measurements and standards. Our leading-edge research and measurements in determining isotopic ratios of carbonaceous gases and volatile organic compounds were used to: 1) identify ozone precursors (produced by exhausts of vehicles vs transpiration of vegetation); 2) finish the program identifying sources of potential organic carcinogens in the EPA's Integrated Air Cancer Project in Roanoke; and 3) continue the comprehensive, integrated aerosol characterization study (species concentration, transport, sources, modelling, etc.) in the Los Angeles Basin. These efforts, made possible through our pioneering research in accelerator mass spectrometry micro-target preparation and chemistry for the determination of carbon isotopic ratios, will lead to the elucidation of the effects of various sources on climate change. Installation and testing of a new gas-ratio mass spectrometer, and research on new isotopic gas standards, strengthens our capability and commitment to provide measurement and standards help in the world-wide problem of global climate change. Several Primary Standard Reference Ozone Photometers used for national and international ozone monitoring, have been updated to include modern computer hardware and software, and have also been calibrated against the NIST primary instrument. Two new photometers were built, tested, and installed in government agencies of Switzerland; we continue to get inquiries from foreign governments about the photometer.

The Chemometrics program, while focusing on the overall concept of Total Quality Measurement, has expanded the standard test data effort to include surface science. Other projects in chemometrics include publication of results in DNA fingerprinting (with the FBI and Div. 831), which defined errors and set specifications, and investigations of neural nets to aid in source identification. Important fundamental work continues on multivariate data structure, quality, fundamental analytical limits (detection, identification, quantification), and accuracy -- closely integrated with and guided by the needs of national and international organizations. A major breakthrough was accomplished in efforts with ISO and IUPAC to obtain a unified

international metrological standard for detection concepts, nomenclature, and practices, with probable future impact on trade, commerce, environment, and health.

Measurement Science - Materials Fabrication/Characterization. An important challenge to various industrial sectors requires understanding the mechanisms of thin-film growth with subsequent improvement of commercial manufacturing techniques. In our magnetic engineering effort, we have investigated the growth, structure and magnetic properties of NiFeCo/Cu multilayers on amorphous silicon nitride using the new Magnetic Engineering Facility. These results were compared with those of commercially grown films; both showed granularity of the layers, with the presence of deep channels that may be the source of Cu "pinholes" and subsequent magnetic shorts in prototypical devices. We are working closely with two ATP awardees (Non-Volatile Electronics, and the National Storage Industry Consortium) to study such problems, the solution of which may lead to higher values of the giant magnetoresistance effect on which magnetic information storage devices are dependent. We have extended related theoretical work reported last year, and calculated the oscillatory exchange coupling between ferromagnetic layers separated by 18 possible spacer metals. While there is qualitative agreement with available experimental data, a more quantitative comparison requires the inclusion of electron spin in the calculations.

The reliable growth of commercial grade high- $T_c$  films is a major obstacle for this important new class of materials that will only be overcome by an increased understanding of surface-related phenomena ranging from growth kinetics to the reactive interactions of the high- $T_c$  film with various underlying substrates. Accordingly, in collaboration with the Univ. of Maryland's Center for Superconductivity Research and the NIST Physics Laboratory, we concentrated on surface studies of single crystal materials as substrates for thin-film growth using ozone-assisted molecular beam epitaxy. We are installing the capability to fabricate and study thin films, junctions and superlattices *in situ* using pulsed laser deposition. These measurements will provide information on how factors such as substrate preparation and morphology, film deposition rate, and temperature affect subsequent high  $T_c$  film characteristics.

Surface Dynamics. In addition to fabricating and determining the morphology and composition of materials and surfaces, we are using novel, state-of-the-art femtosecond spectroscopy and nanosecond lasers, neutron scattering, and radical sources to elucidate the underlying mechanisms of surface reactions induced by photons, ions, and thermal processes.

In our continuing efforts in ultrafast spectroscopy, we have developed the unique capability to probe electronic and lattice coupling strengths over the 280 nm to 5  $\mu$ m wavelength range. By examining the detailed spectral and temporal response of simple adlayer surface systems, we have distinguished between the coupling of low frequency adsorbate modes to carrier and lattice modes of the substrate. This first separation of mode couplings has provided compelling evidence for the applicability of recent models for non-adiabatic coupling proposed at AT&T Bell Laboratories and the University of California (Berkeley). Coupling strength measurements

can provide a direct connection to the fundamental forces involved in adsorbate diffusion and reorientation, of critical importance to understanding surface dynamics and modifications.

Resonance enhanced multi-photon ionization studies on  $\text{Mo}(\text{CO})_6/\text{Si}(111)$  photolysis have confirmed earlier observations of two desorption channels that reflect substantially different dynamics. Additionally, a third novel reaction channel involving defect sites on Si(111) has been identified using state-specific dynamics. This could lead to the identification of defect sites both on "commercial-type" surfaces and in research on defect-free chemical reactivity.

During our efforts to study surface reactions that are stimulated through non-thermal channels, it has become clear that many surface reactions that are not laser initiated involve chemically unstable intermediates that are best treated as chemical radicals. To study these reactions, we have finished an ultrahigh vacuum apparatus centered around a source to generate radical beams photolytically with well-defined kinetic energies in a hyperthermal energy regime. Initial studies will quantify reaction probabilities vs kinetic energy for deuterium and oxygen terminated Si surfaces, and then carbon based radical investigations of low temperature diamond depositions.

Our theoretical study of hot-electron surface femtochemistry has been extended to include the effects of the contributions of the secondary electrons produced, transient chemical bonding, and the presence of different adsorption sites. A combined theory for describing resonant scattering and tunneling of electron wavepackets has also been developed. In all cases, comparisons have been made with experiment.

In the newly added capability of neutron scattering, we (in collaboration with Amoco, Univ. of California - Davis, and MSEL) have characterized hydrogen bound to Ir clusters on and in zeolites X and L. We have begun to correlate the results with extended x-ray absorption fine structure (EXAFS) measurements to identify specific bonding sites. This work will be extended to alternate refrigerants as adsorbates, to determine the dynamics of the refrigerants in the zeolites with the potential of leading to more efficient separations in production processes.

Standard Reference Data and Materials are needed to achieve accurate quantitative measurements. The initial X-Ray Photoelectron Spectroscopy Database, issued in 1989, is being modified to become an easier-to-use Version 2 with additional evaluated data. We have also finished a new series of calculations of electron inelastic mean free paths for 14 organic solids to aid industrial applications of quantitative surface and interface analyses using x-ray photoelectron spectroscopy (in collaboration with Div. 841) and extended the applicability of DTSA for quantitative SEM measurements. Certification of several SRMs were finished this year: SRM 1868-Quantitative Asbestos Building Material, for accurate asbestos identification and quantification; SRM 2063a-Microanalysis Thin Film (Mg-Si-Ca-Fe) to aid in quantitative asbestos and AEM measurements in general; and SRM 2137-Boron in Silicon Depth Profiling to aid in quantitative SIMS measurements on electronic materials. Additional SRM's in progress include Particles-in-Oil, Carbon Isotopic Composition Natural Gas, Microanalysis Particle Composition (spheres), and an Energy Scale Calibration Standard for electron spectrometers.

Members of the Division received several honors this year. Cedric Powell had the distinct honor of having ASTM Committee E-42 name an Award after him; it is to be given to a person "...for outstanding contributions..to..standards for surface analysis." Dale Newbury received the Microbeam Analysis Society (MAS) Presidential Award for "outstanding scientific contributions to the theory and practice of microbeam analysis," and Charles Fiori was posthumously elected an honorary member of the MAS, for scientific contributions to microanalysis only the second person to be so honored. Staff in the Division received two patents and have two others submitted or pending. Strong interactions by the staff with our constituents and effective technology transfer are shown by substantial technical outputs (see Section VI. C), participation on more than 15 editorial review boards, close interactions with national (e.g., ASTM, ANSI, MAS, EMSA, NFPA) and international (e.g., ISO, IUPAC, 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. Ozone Standard Reference Photometer Program**

**J.E. Norris, L.A. Currie, and R.A. Velapoldi**

The tenth year of standard ozone measurements using the NIST produced Standard Reference Photometer (SRP) marked an important expansion in the international network, with the addition of the Swiss Federal Office of Metrology in Bern, and the Swiss Federal Laboratories for Materials Testing and Research in Dübendorf. Our primary SRP serves as the reference standard for 15 units manufactured at NIST and operated by the EPA in their regional laboratories, as well as for an increasing number of foreign agencies. Comparisons among these SRPs conducted this year showed continued agreement to better than 0.5% over the range 0 to 1000 ppbv. In August, we performed an inspection and intercalibration at the Swedish Institute of Applied Environmental Research in Nyköping, where an SRP has been maintained since 1987. This instrument, which has served as the reference standard for ozone measurements in the Tropospheric Ozone Research program in as many as 20 European countries, has maintained agreement to within 0.5% of the NIST primary SRP, after six years of operation in Sweden.

The NIST primary SRP serves also as the reference standard for several U.S. industrial labs that maintain secondary ozone standards. These commercial instruments sometimes show significant deviations from the ideal calibration relationship, including non-linearities, outliers, and shifts of scale. Because of these problems, we have begun work on designed (factorial) experiments to identify potential sources of instrumental error, for improved understanding and implementation of the calibration transfer process.

Also during FY93, work was completed on updating the original SRP control and data acquisition computer to a PC based system, because of the obsolescence of the original Hewlett Packard 85 (HP85) computer. The HP85 has served well for the past ten years, but it has not been produced for five years, and there are few companies that will service these units. The new PC-based system includes all new software that allows considerably more versatility in the control of the SRP's operation, and in the analysis and archiving of the data.

**2. Progress Toward a Unified International Standard for Detection in Metrology**

**L.A. Currie**

A milestone in international metrological nomenclature was reached during FY93 as the outcome of a "landmark meeting" between representatives of the ISO Committee on Measurement Methods and Results (ISO TC-69/SC-6) and the IUPAC Analytical Chemistry Division

(Commission V.1) at the FDA in Washington, DC in July 1993. The meeting was requested by the chairman of the ISO committee, hosted by Bill Horwitz of the IUPAC Commission, organized by L. A. Currie, and chaired by M. Parkany from the ISO Secretariat who also is a member of IUPAC. The meeting represented a unique level of cooperation between the two international organizations on a vital metrological topic in its formative stages. The result was complete harmonization of the fundamental concepts and formulation of approaches and parameters for detection decisions and detection limits in chemical and physical metrology, including calibration, together with major progress toward agreement on the corresponding terms and symbols. (Ref: *Report of the Meeting between ISO and IUPAC on Nomenclature Related to Limits of Detection*, L. A. Currie, Ed., Sept. 1993.)

The importance of a unified international position, by the two organizations having the greatest impact on standards for chemical metrology, cannot be overstated. Meaningful *Detection Limits* lie at the heart of measures for measurement process (MP) capabilities. The ability to specify detection limits is absolutely essential to determine whether an MP will be able to meet certain defined needs for trace substance detection as related to health, safety, or manufacturing/product quality. For some ten years, for example, a part of the World Health Organization, the FAO CODEX Alimentarius Committee on Methods of Analysis and Sampling, has been struggling with the existing morass of definitions and formulations for chemical detection capabilities for food safety. They have now come to IUPAC and ISO for guidance (CX/MAS Commun. 92/10). As indicated in the report of the ISO-IUPAC meeting, "The importance of harmonized international nomenclature for Detection parallels that for harmonized international nomenclature for uncertainty in measurement. Communication and common understanding, especially from the perspectives of international trade, safety, and regulatory practices, lie at the heart of such harmonization." In calling for the meeting, the chairman of ISO/TC-69/SC-6 noted that "... There is an urgent need for answers [to detection limit questions]... In Europe we have a growing number of regulations and recommendations of the European community concerning limits and measurement programs for trace constituents in food, water, air and soil, and almost all lack a reliable background [on] detection limits." [Wilrich, 1992].

### 3. Source Identification of Atmospheric Carbonaceous Species for Urban Airsheds

**G.A. Klouda, D.B. Klinedinst, L.A. Currie, R.M. Verkouteren, L.M. Hildemann (Stanford Univ.), G.R. Cass (Cal Tech), and M.V. Connolly (Albuquerque, NM, Environmental Health Department)**

The Atmospheric Chemistry Group is assisting local municipalities in identifying sources of carbonaceous pollutant aerosols and gases that are not in compliance with the EPA's National Ambient Air Quality Standards (NAAQS). Micro-analytical techniques developed at NIST are used to isolate these substances for <sup>14</sup>C measurements to quantify contemporary and fossil-fuel carbon sources. Such discrimination is essential for cities to design effective control strategies to maintain compliance with the EPA NAAQS for atmospheric pollutants.



In Los Angeles, from the few  $^{14}\text{C}$  reported data of fine aerosols, the amount of fossil carbon seems surprisingly low, given the many industrial sources in the area. It has been suggested that substantial non-fossil organic aerosol may originate from anthropogenically-generated sources such as food cooking operations and wood burning. During the first phase of a collaborative study of this matter, we have: 1) measured  $^{14}\text{C}/^{12}\text{C}$  ratio of aerosol sources in the Los Angeles basin, 2) created an emissions inventory, and 3) predicted contemporary and fossil carbon concentrations using an atmospheric transport model. Results indicate that wood smoke, meat cooking, paved road dust, cigarette smoke, and brake lining wear particles are the primary contributors of contemporary carbon to the LA airshed. Also, there is good agreement between contemporary carbon concentrations predicted and ambient measurements made of Azusa and Long Beach aerosol.

A second study has been completed on the sources of wintertime CO in Albuquerque, NM, to evaluate wood burning and motor vehicle contributions following recent implementation of *no-burn* days based on meteorological forecasts 24 hours in advance. Since this control strategy was initiated in 1988, there has been a substantial decrease in the number of annual exceedances. To evaluate the effectiveness of this control, a factorial (sampling) design, three-factor two-level, was carried out to investigate the following effects: 1) sampling location, residential vs traffic sites, 2) time-of-day, 0630 to 1430 and 1630 to 0030, and 3) forecast meteorology, dynamic vs stagnant air mass. Radiocarbon results for these samples showed that limits to contribution of CO from wood burning ranged from 0% to 41%. For three samples representing forecasted stagnant (*no-burn*) days and the highest CO concentrations, wood burning contributions ranged from 0 to 21%. These results suggest that tighter controls may be necessary for motor vehicles.

#### 4. Database of Methane Isotopic Measurements for Atmospheric Studies

J.M. Conny and L.A. Currie

Tropospheric methane is second only to carbon dioxide in its effect on global warming. Although the tropospheric  $\text{CH}_4$  concentration is a small fraction (5%) of that of  $\text{CO}_2$ ,  $\text{CH}_4$  accounts for about 12% of the global temperature rise, due to strong absorption in a relatively transparent part of the infrared. Intensive  $\text{CH}_4$  measurement and modeling research is underway, because of significant uncertainties in both anthropogenic and natural emission data that are critical for estimating the global  $\text{CH}_4$  budget. In these efforts, isotopic data ( $^{13}\text{C}$ ,  $^{14}\text{C}$ , D, T) are especially important for source identification and quantification. To serve these needs, we have compiled a database of global source and ambient isotopic measurements. Included are: isotopic compositions and uncertainties; sampling times, locations and methods; and sampling and measurement process uncertainties. Emphasis on multi-isotopic signatures and uncertainties provides a basis for assessing the extent to which different  $\text{CH}_4$  emissions or time/space variations in ambient air can be isotopically resolved, given the state-of-the-art in measurement precision. Important observations from the extant database and future research directions are:

- $^{13}\text{C}/^{12}\text{C}$  ratios among the major  $\text{CH}_4$  sources show that isotopic variation due to different bacterial methanogenic processes overshadows measurement imprecision. A better understanding of the effect of bacterial methanogenesis on  $^{13}\text{C}/^{12}\text{C}$  ratios is essential.
- In contrast to  $^{13}\text{C}/^{12}\text{C}$  variation among *different*  $\text{CH}_4$  sources types, D/H variation appears substantially affected by measurement precision. Therefore, D/H resolution of different source types appears limited. However, D/H ratios are important for distinguishing different methanogenic mechanisms controlling emissions from *individual* source types.
- Among non-fossil sources (wetlands, ruminants, biomass burning), boreal peat bogs, because of the greater age of the organic substrate, exhibit lower  $^{14}\text{C}$  activities than tropical wetlands. Thus,  $^{14}\text{C}$  holds promise for latitudinal wetland discrimination.
- Using empirical regression models, we shall attempt to predict characteristic isotopic signatures of wetland  $\text{CH}_4$  from different latitudinal zones and/or vegetation communities.
- Using existing emission databases for the three major  $\text{CH}_4$  sources (wetlands, rice paddies, ruminants) which are highly resolved geographically ( $1^\circ \times 1^\circ$ ), we shall establish a global database containing multi-isotopic source signatures for each  $1^\circ \times 1^\circ$  cell.

## 5. Successful Technical Oversight and Transfer to Industry of Asbestos Measurements

E.B. Steel, J.R. Verkouteren, E.S. Windsor, D.J. Hues, and S. Turner

By the Asbestos Hazard Emergency Response Act of 1986, Congress mandated that the nation's schools be tested for the presence of asbestos. In this legislation, Congress also mandated that NIST develop accreditation programs for those analytical laboratories applying the methods specified by the Environmental Protection Agency to detect the presence of bulk and airborne asbestos. Accreditation is awarded by the National Voluntary Laboratory Accreditation Program (NVLAP) at NIST. The Microanalysis Research Group (MRG) has provided technical expertise to NVLAP to develop the accreditation program and has had the major responsibility for developing accurate measurement methods, proficiency testing procedures, and materials used in proficiency testing as well as developing and certifying SRMs used by the testing laboratories.

Bulk Asbestos Accreditation Program: Technical maintenance of this program has been successfully transferred to the Research Triangle Institute (RTI) and we have assumed the oversight role for quality assurance. To reach this goal, we worked closely with RTI to transfer the appropriate reference measurement methods, and developed a data collection and

recording format to enhance the quality assurance procedures. Two proficiency tests have been conducted successfully since the transfer of the major technical responsibility to RTI. Under the current agreement, the MRG and RTI plan the proficiency test (timing, materials and procedures to be tested), RTI performs the primary characterization of the materials, assigning reference material values and determining homogeneity, MRG analyzes a small subset of the materials and the results are compared statistically with RTI's results. Approximately 500 laboratories are tested; they return their results of the proficiency test to RTI for entry into the database. The MRG and RTI evaluate the laboratory results, taking into consideration every aspect of the proficiency test, including testing directions, reference materials, and even additional material testing. Pass/fail criteria are determined collaboratively among the MRG, RTI, and NVLAP with input from statisticians. In addition to maintaining our quality assurance oversight role, we continue to check test reports, as well as respond to laboratories seeking technical advice.

Airborne Asbestos Accreditation Program: In this program, the developmental phase of the proficiency testing program is ending, and the transfer of the major responsibility, similar to the bulk asbestos accreditation program, will be accomplished during the next year. In the developmental phase, we tested the ability of the more than 100 laboratories participating in the program to make accurate measurements using the analytical electron microscope. This has included testing their knowledge of measuring d-spacings in diffraction patterns, their ability to identify X-ray peaks, determine resolution, and sensitivity factors (k-values) using energy dispersive spectrometry, their ability to identify unknown samples, and their ability to count and analyze asbestos on grids and filters. The variety of tests that we devised has allowed us to determine the strengths and weaknesses of the laboratories and the measurement procedures. We have used the results to instruct the laboratories in the use of correct procedures.

In this program, we have designed the tests, developed instructions and forms, tested the instructions and the laboratories, analyzed the materials used in the tests, evaluated the results, established pass/fail criteria, and written the summary and individual reports. In the present proficiency test (and in future testing), we intend to establish a routine in which the laboratories prepare and analyze asbestos on filters (and grids) for one test, and perform verified asbestos analyses on the grids prepared by other laboratories for the second test. This standardization will enable us to transfer the major responsibility to a contract laboratory while we provide quality assurance oversight for the program.

## 6. Micro-Scale Real-Time Imaging of Alpha Radioactivity

**C.J. Zeissler**

A radiation imaging system based on a CID (charge injection device) camera and desktop computer is being applied to real-time imaging of alpha-particle radioactivity. The Video

Radiation Detector (VRD) thresholds, displays and actively integrates the charge deposited by alpha particles in a 512 x 480 pixel array at the rate of thirty frames per second. The efficiency is approximately 100% over a 2-ip steradian collection geometry without any focusing or conversion mechanisms. The position of alpha-emitting point sources can be located with an accuracy of approximately 25 micrometers or less, dependent on counting statistics. The high efficiency and spatial sensitivity are achieved by applying the sample directly to the surface of the detector. The maximum sample size is limited to 7 mm x 9 mm per exposure. A background of only 2 or 3 randomly spaced counts per day and unlimited total integration periods make the detection sensitivity limited only by the patience of the analyst. For example, a week-long count can locate a point source emitting only  $1.6 \times 10^{-5}$  Bq, or  $4.5 \times 10^{-16}$  Ci. Although degradation of the signal-to-noise ratio has been observed at 5 MeV alpha doses in excess of 0.5 dpm per 0.5 square mm surface area (50 dpm total), our applications and sample types do not involve this much activity. "Contact print" images of the sample made with visible or infrared illumination can be used to correlate radioactivity images directly with the physical details in the sample and registration marks on the sample substrate. Count rates for each individual alpha source in a sample are easily obtained, and with size observations and spectrometry results, nuclide concentrations can be estimated. VRD results can also be used to prepare samples, and to augment and direct subsequent microanalysis by optical, electron or ion beam methods.

In comparison to conventional track-etch methods, the VRD takes the guess-work out of how long to expose a sample because it is a real-time method, and the VRD does not require chemical processing and optical scanning. Additionally, the digital results of the VRD are quickly interrogated to determine individual count rates, source positions and dose or dose-rates on any user-selected area. Conventional track-etch methods, however, can complement the efficiency of the VRD as a prescreening method when the task is to locate "hot particles" in large particulate sample masses that have less than 1 dpm alpha activity per mg of particulate. For sources thus prelocated, or for sample activities in excess of 1 dpm/mg, direct use of the VRD is more advantageous. The VRD has been applied to the location and preliminary analysis of plutonium, polonium, americium, thorium and uranium-bearing particles and fibers in reference materials, minerals, and environmental samples.

## 7. Fourier-Transform Micro-Raman Spectroscopy of Microsamples

E.S. Etz

Infrared and Raman vibrational spectroscopies provide analytical information that cannot be obtained from other microprobe techniques, including molecular bonding and structure, species identification, and major to minor molecular composition. With the installation during FY93 of a comprehensive macro-/micro-Fourier transform (FT) infrared and Raman system, a new range of analytical capabilities has become available in the microprobe area. Prior to this time, our research in micro-Raman spectroscopy was confined to the excitation of Raman spectra

with laser sources (e.g., argon and krypton ions) in the visible region, employing conventional dispersive Raman spectrometer systems with either photomultiplier or optical array detection. The new FT-Raman system employs excitation in the near-infrared (diode pumped Nd:YAG laser at 1064 nm,  $9394\text{ cm}^{-1}$ ) using interferometric instrumentation to provide the advantages of increased throughput, multiplex characteristics, and precise spectral frequency measurement. The most important feature of near-IR Raman spectroscopy for the analysis of a wide range of materials is the virtual absence of laser-excited sample luminescence, which is often troublesome for spectra in the range from  $\sim 450$  to  $\sim 750$  nm. Even with red light excitation (e.g., at 647.1 nm, Kr-ion), luminescence interferences arising from either sample chromophores or trace impurities may often totally mask the intrinsically much weaker Raman spectrum. A second potential advantage of FT-Raman spectroscopy with near-IR excitation is a reduction in laser-induced sample heating and photodecomposition, especially for Raman microsampling. The microanalytical capabilities of the new FT-Raman system have been broadly explored in measurements on samples heretofore difficult (or impossible) to characterize by conventional Raman methods. These studies encompass various classes of synthetic and natural polymers and resins, composites and ceramics, a range of polycyclic aromatic hydrocarbons (PAHs), various explosives and drug substances, some organometallics and coordination complexes, and selected biologicals and biomedical materials. These have been analyzed in the form of either particles, microcrystals, thin films or layers, or at interfaces and fracture surfaces. Specific examples of materials in some of these categories that now furnish excellent Raman spectra are aramid (Kevlar) and polyimide (Kapton) fibers and films, the explosives HMX, RDX, and PETN, metal-containing porphyrins, and biological thin sections of calcified tissues (e.g., atherosclerotic plaques). Other current investigations center on the study of CVD diamond films and wafers where the new FT-Raman spectra provide increased sensitivity for the detection of non-diamond ( $sp^2$ -bonded) carbon resonantly enhanced at  $1.064\text{ }\mu\text{m}$ . These results substantially augment our efforts toward the development of a Raman spectroscopic standard for the CVD diamond industry.

## 8. Assessment of Silicon Wafer Cleaning Procedures by Secondary Ion Mass Spectrometry

**D.S. Simons, P.E. Thompson (NRL), and D.J. Godbey (NRL)**

Successful growth of epitaxial silicon by molecular beam epitaxy (MBE) requires that the surface oxide on the substrate as well as other impurities be removed prior to growth. Standard cleaning procedures have been developed, one of the most common being the "Shiraki" process. Concerns about the high temperature required for this process and the residual boron remaining on the surface have stimulated investigations of alternative cleaning processes. In this study we compared the results of a full Shiraki clean, an abbreviated Shiraki clean, and a simple dip in 4% HF. An additional variable investigated was whether the wafer was baked prior to MBE growth. After cleaning and baking, about  $0.28\text{ }\mu\text{m}$  of MBE Si was grown on each wafer.

The samples were profiled for impurity content by secondary ion mass spectrometry (SIMS). The species H, C, O, F, and N (as SiN) were monitored as negative secondary ions under Cs<sup>+</sup> bombardment at an impact energy of 14.5 keV. The species B, Al, Cr, and Ge were monitored as positive secondary ions under 5.5 keV O<sub>2</sub><sup>+</sup> bombardment. For the Cs primary beam profiles, ion-implanted samples of C and O in float-zone Si were used to investigate the analytical conditions that would produce the lowest detection limits. The sample chamber pressure was about 3x10<sup>-8</sup> Pa and the samples were in the chamber for at least 12 hours prior to analysis. The best detection limits for C and O were obtained with a Cs<sup>+</sup> current of 50 nA, a raster size of 50 x 50 μm, an accepted area of secondary ion extraction 30 μm in diameter, a sample voltage offset of 30 V, an energy acceptance window of 50 eV, and the sample chamber cold trap chilled with liquid nitrogen. Under these conditions, the detection limits for both C and O, as determined from the backgrounds in the implanted float-zone Si, were 5x10<sup>16</sup> atoms/cm<sup>3</sup> (1 ppm atomic). The sputter rate was about 9 nm/s. If only a single species was monitored for 0.5 s/cycle, the data spacing was 4.5 nm.

For the MBE samples, each of the species H, C, N, O, and F was monitored in separate profiles using the conditions detailed above. Concentration scales for C and O were based on relative sensitivity factors (RSFs) determined from implanted samples. For H, N, and F, tabular values of RSFs were used. The Shiraki-cleaned sample had the lowest levels of C, N, O, and F at the interface with the original surface of all samples investigated. However, it did show factors of 10 to 100 more B at the interface than any of the other samples. The HF-dipped sample with no bake had the highest interfacial impurities for C, N, O, and F, but a factor of 10 lower B than the Shiraki-cleaned sample. In this study, we demonstrated that high-performance dynamic SIMS has the capability to detect cleaning residues on Si wafers, with sheet densities in the range of 10<sup>9</sup>/cm<sup>2</sup> in favorable cases.

## 9. High Spatial Resolution Isotope Ratio Imaging Using Secondary Ion Mass Spectrometry

G. Gillen and D.S. Bright

Isotope ratio imaging is a very powerful but as yet underutilized analytical capability of Secondary Ion Mass Spectrometry (SIMS). With recent advances in SIMS imaging systems, it is possible to generate isotopic images with high mass resolution and high spatial resolution. The ability to characterize precisely the composition of isotopically heterogeneous materials on a micrometer spatial scale has many potential applications, including biological tracer studies, studies of atmospheric particles, and identification of isotopic anomalies in geological and cosmological materials. We are studying the feasibility of high spatial resolution isotope ratio imaging using an ion microscope SIMS instrument (Cameca IMS 4F) equipped as an ion microprobe. In this mode, the spatial resolution of the image is dependent on the spot size of the primary beam, which for the 15.0 keV O<sub>2</sub><sup>+</sup> bombardment used in this study, was 0.25 micrometers (with a Cs<sup>+</sup> primary bombardment probe, sizes of ~0.1 micrometers are possible).

Our initial experiments with microprobe imaging have focused on isotope ratio imaging of 5 NIST prepared research glass standards doped with lithium. Each of these glasses has a different  ${}^6\text{Li}/{}^7\text{Li}$  ratio (21.6, 1.132, 0.477, 0.193, 0.084). The glasses were ground into fine particles and dispersed onto a carbon planchette with cyclohexane. Images of  ${}^6\text{Li}$  and  ${}^7\text{Li}$  were obtained from a variety of areas on the sample. We were able to identify the different isotopic compositions of these samples even from particles as small as 1 micrometer. To display the isotopic ratio images in a meaningful way, we need to present simultaneously both spatially resolved information and quantitative intensity data to the observer. One way to do this is by using a transformation called Concentration Histogram Imaging (CHI). To generate a CHI, we start with two registered Li isotopic images, each represented by an array of pixels(x,y), each pixel giving one intensity value for each isotope at location x,y. The CHI is constructed by incrementing an element of the histogram image array h(i,j) where i and j correspond to the values of intensity for every location (x,y) in the two isotopic images. After the CHI array is calculated, we display it as an image using a thermal scale. This concentration histogram image allows us to identify quickly the isotopic composition of the sample. Also, we have found the CHI to be very useful for identifying the detector dead-time effects that may lead to erroneous isotopic ratio measurements. In addition to the lithium glasses, we have also been studying the imaging of magnesium isotope ratios from B1 Ca-Al-rich inclusions in the Allende meteorite. These inclusions have been found to have  ${}^{26}\text{Mg}$  excesses of 5-15%. Typically we acquire alternate images of  ${}^{26}\text{Mg}$  and  ${}^{24}\text{Mg}$  (to minimize variations in signal drift) which are summed after the analysis. Total counting times are typically 30 min for  ${}^{26}\text{Mg}$  and 10 min for  ${}^{24}\text{Mg}$ . If desired, we can correct for dead-time effects, mass bias, and hydride interferences on a pixel-by-pixel basis. For these samples, because of the high secondary ion signal of Mg, it is possible to collect signals for the minor isotope exceeding 20,000 counts/pixel. This allows us to achieve a precision of better than 0.7% on an individual pixel. We have found enrichment in the  ${}^{26}\text{Mg}$  of 6.0-10.0% in various grains of the meteorite sample.

#### 10. Elemental and Isotopic Characterization of Sub-Micrometer Particulate Material by Time-of-Flight Secondary Ion Mass Spectrometry

J.A. Bennett and D.S. Simons

Secondary ion mass spectrometry is an inherently destructive analytical technique that requires the irreversible consumption of material during analysis. For the vast majority of applications, the consumption of material does not present a problem because the sample is present in a bulk form that provides sufficient material for several analyses. However, as the size of the sample decreases, the volume of material available for consumption also decreases. Therefore, acquisition of precise and accurate data from single sub-micrometer particles will be closely tied to the efficient use of consumed material. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a highly efficient method for obtaining elemental and isotopic information from volume-limited samples. In TOF-SIMS, secondary ions created during a single sputtering event are detected in parallel. Mass separation is accomplished without the aid of scanned magnetic

or electric fields thereby resulting in inherently high transmission efficiencies (10% or greater). These two features, but in particular the parallel detection capability, allow TOF-SIMS to extract the maximum amount of information from volume-limited samples. Fast mass switching methods and improved transmission efficiencies have made state-of-the-art magnetic sector SIMS instruments capable of obtaining accurate and precise isotopic information from micrometer size samples. However, as the sample size decreases and/or the number of isotopes to be monitored increases, the ability to monitor several isotopes simultaneously becomes an important advantage in quantitative measurements. We are currently evaluating the capabilities and limitations of TOF-SIMS for obtaining elemental and isotopic information from sub-micrometer size particulate material. The TOF-SIMS is equipped with a highly focusable, liquid metal ion source capable of producing a primary ion beam approximately 0.25  $\mu\text{m}$  in diameter. This facilitates the selection of particles for detailed analysis. We have successfully demonstrated the ability to relocate and analyze particles transferred between an analytical electron microscope (AEM) and the TOF-SIMS. The AEM provides quantitative elemental information prior to measurement of isotopic ratios. We are currently addressing issues related to ultimate detection limits, as well as the precision and accuracy of the TOF-SIMS method, as a function of particle size. Preliminary data collected from thin film standards showed useful yields for Mg and Ca to be 0.0057 and 0.012, respectively. The useful yield is defined as the number of ions detected per atoms sputtered and is dependent on ionization, transmission, and detection efficiencies. These useful yield values suggest that a statistically meaningful secondary ion signal ( $>100$  counts) can be obtained from as few as 20,000 atoms of Mg and 10,000 atoms of Ca. We intend to test whether or not these predicted sensitivities extend to sub-micrometer particulate material.

11. Patterning of Self-Assembled Alkanethiol Monolayers on Silver by Microfocus Ion and Electron Beam Bombardment

J.G. Gillen, S.A. Wight, J.A. Bennett, and M. Tarlov (836)

The formation and characterization of self-assembled monolayers (SAMs) of alkanethiol molecules on metal surfaces (Ag, Au, Cu, GaAs) are active areas of research. The interest in SAM films stems from their ease of preparation, high quality, and stability. Most importantly, the chemical functionality of the surface of these films can be easily manipulated by variation of the terminal functional group of the thiol molecule. The capability to prepare organic films with tailored surface chemistries is important for fundamental studies of organic surfaces and may also lead to numerous industrial applications. Recently, several groups have demonstrated that it is possible to pattern two or more of these monolayers onto metal substrates using mechanical or photochemical techniques. The ability to fabricate discrete patterns of molecules on surfaces, each with specific chemical, biological, or adhesive properties, opens even more possibilities for the technological application of these materials. For example, patterned SAMs could find use as biosensors, corrosion barriers, and resists for semiconductor device manufacture. Our research is focused on development of alternative strategies for patterning



of self assembled monolayers on surfaces. One promising approach is the use of microfocus ion or electron beam bombardment for pattern generation. The potential advantages of this approach are universal applicability to all types of SAM films and higher spatial resolution than currently available with photolithographic or mechanical techniques. Initial evaluation of this process has been carried out using either our TOF-SIMS instrument equipped with a Ga<sup>+</sup> liquid metal ion gun or a JEOL 840 scanning electron microscope. To generate a monolayer pattern, an alkanethiol monolayer sample is bombarded with a highly focused, continuous primary gallium ion beam (or electron beam) rastered over a small area of the sample in various patterns. After bombardment, the sample is removed from the instrument and immersed for 1 minute in a solution of a second alkanethiol molecule. This immersion results in the bonding of the second monolayer species to the regions of the metal film where the first monolayer was removed by the ion or electron bombardment. The result is a pattern on the surface consisting of two different molecules, each with different chemical functionality. Individual features with dimensions of a few micrometers have been generated using this technique. We have also found that as the dose of the Ga ion beam and electron beam increases, the extent of exchange of the second thiol molecule also increases until a plateau is reached. A detailed study of this effect is now underway.

## 12. Advanced Processing of Particle X-Ray Spectra for Automated Analysis

**J.A. Small**

Advances in electron beam instrumentation and computer-controlled automation have led to the development of automated scanning electron microscopy (ASEM) which permits extensive x-ray spectral data to be collected from thousands of individual particles during unattended operation. Experimental results indicate that the reduced precision associated with the shorter counting time analyses severely limits the ability to distinguish correctly among elementally similar groups of particles. A second potential problem with automated analysis is poor accuracy resulting from the fact that the x-ray data collected on individual particles during an analysis are not corrected for particle-size and -shape effects which substantially modify the measured intensities. The reduced accuracy may lead to incorrect identification of particle groups and misinterpretation of ASEM results.

To study the accuracy associated with quantitative particle analysis methods, a series of six closely spaced glass compositions was prepared by substituting Fe for Si in a SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO-MgO-TiO<sub>2</sub>-FeO glass, giving a range in the Fe concentration from 0.7 to 7.0 weight percent. This series was chosen because the glass compositions are relatively easy to analyze quantitatively. Only minor peak overlaps occur which can easily be handled by existing software, and all the elements can be analyzed by K-shell x-ray lines for which the various analytical parameters are well known. Irregularly-shaped particles in the 1-50 micrometer size range were prepared by wet grinding the glasses. X-ray spectra were collected while

overscanning the particles, and analysis times were selected to minimize the uncertainties associated with counting statistics.

The results from three different particle-correction methods were compared with the "true" composition as determined by the analysis of the corresponding bulk glass: (1) simple normalization of the conventional ZAF matrix corrections as measured against bulk standards; (2) geometric corrections based upon the local peak-to-background ratio; and (3) the Armstrong-Buseck particle geometry factor method based upon modeling electron/x-ray interactions. The performance of the different correction procedures for ASEM analysis was evaluated with the composition histogram plots of Fe vs Si and the resulting particle clusters. Preliminary results indicate that the Armstrong-Buseck algorithm has a slight advantage over the other correction procedures for the 7% Fe glass only, while the results from the other glass concentrations indicate that the accuracy of the different correction methods is comparable. These observations suggest that a simple normalization of the results from the conventional ZAF/bulk standards correction procedure can provide adequate accuracy for most ASEM particle characterization studies.

### 13. Quantitative Wavelength Dispersive Spectrometric Analysis

#### R.B. Marinenko

In collaboration with an industrial company (Noran), we have carried out a detailed evaluation of a new x-ray electronic counting system for the flow-proportional and xenon sealed detectors of the wavelength-dispersive spectrometers incorporated in an automated electron probe microanalyzer. Several parameters critical to high accuracy analysis were characterized: (1) The x-ray pulse counting dead time was determined for the new electronics on each of the five spectrometers using two elements with x-ray lines at the low and high-energy end of each crystal. Although the dead times varied slightly from one element to the next, they were all less than 1  $\mu$ s, and, most importantly, these values could be reproduced. (2) Different discriminator window settings were used and, (3) detector biases were examined. In the past our laboratory has used open or integral discriminator windows with a lower discriminator setting at 0.2 V to eliminate low-energy noise pulses and sometimes an escape peak. The upper level was set at 10 V and the x-ray pulses from the detector were set at 4 V (well within the window) by adjusting the bias voltage on the detector. Other discriminator and bias settings were investigated to determine if they could improve quantitative results. Two other discriminator windows known to be used in the electron microprobe community were tried. These were the differential 2 V (0.35 - 2.35 V) and 4 V (1 - 5 V) windows. The detector bias was adjusted in both cases so that the pulses occurred in the middle of the window. High-energy noise and pulses from higher-order x-ray lines can be excluded when the upper discriminator setting is lowered. Analysis of SRM 479a steel, with a nominal composition for iron, chromium, and nickel of 71, 10, and 19 weight percent, respectively, gave the same quantitative results with all three discriminator settings. However, analysis of a steel specimen

containing less than 1 weight percent silicon gave unsatisfactory results for both of the differential windows when using high count rates. This was caused by a shift to lower energy of the x-ray pulses from the pure silicon standard than the silicon pulses from the unknown steel. This is a well-known phenomenon which causes either the standard or unknown to fall outside of the discriminator window. It is a strong justification for using an open discriminator window for routine quantitative analyses. These systematic measurements have demonstrated that the new equipment provides a marked improvement over the original counting electronics. The time spent on understanding the equipment and how to properly set it up has improved the accuracy of quantitative WDS analyses, especially when high counting rates are desired, as is the case for operation in the compositional mapping mode.

#### 14. Examining Particles Directly on Filters with Environmental Scanning Electron Microscopy on Filters

S.A. Wight

Conventional (high vacuum) scanning electron microscopy is often severely challenged to image particles on filters. Most filter materials are insulating and tend to accumulate the surface charge that the beam deposits, leading to localized charging. Unprepared particles often acquire a surface charge under the beam of like sign to the substrate and "jump" off the filter material due to electrostatic repulsion. The most common approach to reduce the effects of charging is to coat the filter and particles with a conductive layer (C, Au, Al, etc.) before investigation in the SEM. While such a procedure can improve the stability under electron bombardment for imaging and x-ray microanalysis, coatings can compromise the particles for subsequent examination by another analytical method. For tortuous path filters and/or complex particle aggregates, coated samples examined in conventional SEMs are completely inadequate.

The evolution of a new, commercially available scanning electron microscope has opened a new option for particle microscopy. The environmental scanning electron microscope (ESEM), also referred to as high pressure or low vacuum SEM, allows the investigation of virtually any sample (wet, insulating, and uncoated). The ESEM operates from high vacuum up to about 500 Pa (~4 Torr) and takes advantage of the gas molecules present to provide charge neutralization as well as the imaging signal through an ionization cascade. The ESEM provides image formation with secondary or backscattered electrons and x-ray analysis by energy dispersive or wavelength dispersive spectroscopies. To establish "proof of principle" of the applicability of the ESEM for the challenging problems presented by particle samples, a series of experiments was performed at the demonstration laboratories of commercial ESEM manufacturers. Various particle/filter combinations examined in the ESEM included: fly ash particles on a polymer substrate, aerosol particles collected on an open-faced Teflon filter, aerosol particles collected by an impactor onto a Teflon filter, aerosol particles collected onto a polycarbonate membrane filter, and polystyrene latex spheres deposited on a paper filter and a glass slide. Under ESEM conditions, stable images of particles with high spatial resolution

were easily acquired for these cases. Comparison images of these specimens obtained under conventional high vacuum conditions in the same instrument confirmed the advantage of ESEM operation.

## 15. MacLispix: a Macintosh Application for Image Analysis

**D.S. Bright**

MacLispix (MLx) is an image processing software engine based on Macintosh Common LISP with functions added for image manipulation and display. It is more flexible than other Macintosh image processing applications for adding special data types and special purpose algorithms. Images are represented as LISP arrays and the pixels can be of almost any data type (for example bytes, large integers, real, rational or complex numbers). The arrays can be allocated dynamically, and the pixel values can be accessed easily. MLx is unique in this respect. MacLispix displays images with 8 bits (one byte) of gray scale information. Color overlays can be made of two or three gray scale images and displayed as 24 bit color (or, automatically by the system as 8 bit color if a 24 bit screen is not there). Displayed images are linked back to original array values for analysis. Two- and three-dimensional Concentration Histogram Image (CHI) capability with traceback is provided. MLx takes advantage of the Macintosh graphic user interface by using menus, dialogues, and graphics where appropriate. Information is extracted from images by locating positions or areas with the mouse. MLx can read a number of specialized file formats, for handling images from a variety of analytical instruments, and then write the images in a more generic format. MLx also has provisions for making slides: images can be resized, labels made, a background chosen and the menu bar removed. Multiple images can be displayed in this "photo mode", in contrast to two more widely used image processing packages which allow display of only one image in this mode. False color scales include a flexible thermal scale, and multiple color bands used for thresholding images and determining values and ranges of data. Many numeric operations are available, as well as convolutions with various kernels for smoothing, edge enhancement and the like. Ratio images can be made, taking into account special restrictions for noise suppression. High precision integer arrays can be read and stored. This feature has been used for summed images containing isotope ratio data. Various means of scaling, that have proved useful in other image processing systems used by the group, have been included. MLx is also designed as a tool for algorithm development and exchange. The source code is easy to access and to change. The LISP code can be changed and tested in a short time with the application still running and the images still loaded. Macintosh Common Lisp, in which MLx is embedded, also has facilities for self documenting code, listing defined functions, completing partially typed words automatically, and searching source code files. MacLispix (MLx) was developed for use by the Microanalysis Research Group to enhance and extract data from micrographs and elemental maps of various materials and biological samples. It is a research tool under continual development. The application, documentation and source code are available without charge.

## 16. Desktop Spectrum Analyzer: Accuracy of First Principles X-ray Spectrum Simulation

D.E. Newbury, R.L. Myklebust, and C.R. Swyt (Guest Scientist, NIH)

Desktop Spectrum Analyzer (DTSA) is a comprehensive software engine for the collection, peak deconvolution, background subtraction, quantitative matrix correction, simulation, and database processing of electron-excited x-ray spectra for use with the electron probe microanalyzer, analytical scanning electron microscope, and analytical electron microscope. One of the most powerful aspects of DTSA is the "first principles" simulation of x-ray spectra, which takes into account the physics of generation, propagation, and measurement of characteristic and continuum (bremsstrahlung) x-rays with an energy dispersive spectrometer (EDS). The simulated spectrum can be viewed at each step of the process: (1) the primary characteristic radiation and the x-ray continuum as generated within the target; (2) after undergoing absorption in the specimen while propagating toward the detector; (3) with the additional secondary fluorescence radiation as a consequence of absorption; (4) after propagation through the detector windows and structure, including transmission; (5) after the action of the spectrometer measurement process that results in peak broadening; and (6) after the application of random counting statistics. One important use of DTSA spectral simulation is to estimate whether a minor or trace constituent can be detected in the x-ray spectrum measured from a particular matrix composition. Traditionally, this problem has involved actually measuring a material of the appropriate composition to examine the region of the spectrum where the x-ray peak(s) of interest for the trace/minor constituent would exist to determine a limit of detection. Unfortunately, a suitable standard with an appropriate composition that is homogeneous at the micrometer level is not usually available for a direct measurement to make such a determination. DTSA can now be used to simulate a spectrum for the assumed composition. Random counting statistics can be applied to this simulated spectrum, and then the characteristic peak intensities can be recovered by deconvoluting with multiple least squares peak fitting or with the sequential simplex Gaussian peak fitting procedure. This simulation/deconvolution sequence can be repeated with different random counting statistics to simulate repeated measurements or to simulate longer counting times. From such "Monte Carlo" studies, a statistically valid estimate of the limit of detection for the constituent(s) of interest can be obtained. Such information can then be used to modify the selection of instrument operating conditions, e.g., the beam energy, dose, counting time, etc., so as to improve the detection situation. The accuracy of such a procedure is obviously dependent on the accuracy of the spectrum simulation. Detailed experimental measurements and DTSA simulations of standards containing elements producing complex spectra involving K, L, and M shell x-rays have shown that spectral intensities can be predicted from first principles within  $\pm 20\%$  relative in most cases.

## 17. Trace Nanoanalysis Characterization of Ceramic Nanoparticles

D.E. Newbury

Trace nanoanalysis, the detection of highly diluted elemental species at the parts per million atomic (ppma) level while simultaneously localizing the measurement to a lateral spatial resolution at the nanometer scale, can be achieved by analytical electron microscopy with parallel detection electron energy loss spectrometry (AEM/PEELS). Numerous elemental species, including the alkali metals, alkaline earths, transition metals, and rare earths, are accessible by AEM/PEELS. The development of trace nanoanalysis permits an analyst to address entirely new questions about the microstructural distributions of trace constituents. With conventional AEM/energy dispersive x-ray spectrometry (EDS), only trace constituents that are localized at concentrations greater than one weight percent can be readily measured, and only then if the particular sites of localization can be discovered through searching, which generally requires a large investment in instrument time even with efficient automation. For those elements accessible at trace levels by AEM/PEELS, the presence of trace constituents can be determined at every location in a microstructure or in every particle of a dispersion. By combining the high localization of AEM/PEELS with conventional bulk trace techniques such as neutron activation analysis, comprehensive characterization of the distribution of trace constituents becomes possible. This analytical strategy has been applied to the characterization of nanoscale magnetic ceramic particles produced by NIST and by industrial collaborators. In one example the fate of a trace dopant added during the synthesis of nanometer-scale particles was of particular interest. Bulk trace analysis techniques confirmed the successful overall doping of the particle sample, but the magnetic properties of this particulate material revealed anomalous behavior inconsistent with the doping. Initial examination of individual particles in the size range of 5 - 50 nm by AEM/PEELS showed that the trace dopant, measured to levels below 100 parts per million atomic, was not uniformly distributed. Repeated analyses of several hundred particles eventually revealed the localization of the dopant at much higher concentration in a few particles, and also showed the completely unexpected contamination of those particles with tungsten from the high temperature evaporation apparatus. The combination of trace nanoanalysis and bulk trace analysis was vital to developing a proper understanding of the materials fabrication process.

## 18. Subpicosecond Laser Measurements to Separate Electronic and Phonon Coupling

T.A. Germer, R.R. Cavanagh, E.J. Heilweil (PL), and J.C. Stephenson (PL)

The exchange of energy between a solid and an adsorbed layer is critical for understanding processes ranging from novel radiation-induced surface chemistry to more common events such as thermally activated diffusion. Most of the current insight into the relevant factors in energy transfer arises from theoretical models. However, different models vary by orders of magnitude in their estimation of the critical time frame for such processes. There is a striking

need for experimental benchmarks that can establish the relevant time frames and energy transfer mechanisms for simple systems that can further be compared to existing theoretical models. Through such comparison, it will become feasible to establish the validity of competing models and to advance the current understanding of chemical modification of surfaces and interfaces. Using subpicosecond pump-probe spectroscopic techniques, we have been able to follow the evolution of energy initially deposited in a copper substrate and to also address the time scale and mechanism involved in transferring that energy to the adsorbate bonds.

The measurements were made with a half monolayer of CO bound to Cu(100). The surface is initially excited by a 100  $\mu\text{J}$  pump pulse at 578 nm. A time-delayed picosecond probe pulse centered at 2086  $\text{cm}^{-1}$  (15  $\text{cm}^{-1}$  FWHM) was spectrally dispersed after reflecting from the surface. A marked shift in the CO stretch mode near 2086  $\text{cm}^{-1}$  was apparent. This shift was attributed to activation of the 32  $\text{cm}^{-1}$  frustrated translational mode of the Cu-CO bond. By examining the temporal dependence and extent of that shift, the time scale and magnitude of activation of the frustrated translational mode have been addressed. Absorption of the visible pulse initially excites electrons in the metal, and on a 1.5 ps time scale the electrons equilibrate with the phonons, resulting in thermal heating of the crystal. In the first few picoseconds after the arrival of the excitation pulse, the electronic temperature is significantly greater than the surface lattice temperature. Through the temporal resolution afforded by these measurements, it has been possible to follow the coupling of this electronic transient to the adsorbed CO and to establish quantitatively the coupling strength of the excited electron and phonon modes to the adsorbate bond.

Our results are accounted for by coupling times for the frustrated translation of  $4\pm 1$  ps for the lattice phonons and approximately  $5\pm 1$  ps for the excited electrons. The comparable magnitude of the two coupling strengths indicates that both lattice and electronic degrees of freedom must be considered when adsorbate/substrate energy transfer is being addressed. Theoretical models for these dynamical processes have recently been developed at AT&T Bell Labs and the University of California at Berkeley, where *ab initio* treatments are in excellent agreement with both the measured time scale and importance of electronic and lattice degrees of freedom. The ability to establish limits on these two coupling strengths independently is providing valuable guidance in modeling both diffusive and nonthermal surface processes.

## 19. Photodynamics of $\text{Mo}(\text{CO})_6/\text{Si}(111)$ : Defects, Islands, and Multilayers

**P.M. Chu, S.A. Buntin, L.J. Richter, and R.R. Cavanagh**

To exploit lasers to drive selective, low temperature surface processes, it is essential to understand reaction and energy transfer pathways of adsorbates on surfaces. In deposition systems the relevant adsorbates are typically organometallic, metal-center molecules. Ideally, the laser radiation will strip away the ligands, which desorb into the gas phase, leaving behind a patterned layer of metal atoms. In reality there are a number of competing pathways, such

as energy transfer and ligand interactions, that interfere with this ideal picture. To serve as a model system in the characterization of laser-induced deposition, the photodecomposition dynamics of  $\text{Mo}(\text{CO})_6/\text{Si}(111) 7 \times 7$  have been probed by applying state-selective detection techniques to the evolved CO photoproduct.

Our previous studies of this system relied on vacuum ultraviolet laser-induced fluorescence detection of the photofragment CO. Due to sensitivity constraints, it was only possible to probe the dynamics in the multilayer regime. To enhance the experimental sensitivity and allow evaluation of the dynamics in the monolayer regime, we have employed a resonance-enhanced multi-photon ionization scheme to detect CO. This sensitivity improvement is quite significant since it has allowed the characterization of the  $\text{Mo}(\text{CO})_6$  photodecomposition dynamics in all coverage regimes.

Results for  $\text{Mo}(\text{CO})_6$  adsorption at 100 K on a sputter/annealed prepared  $\text{Si}(111) 7 \times 7$  surface typically show three CO desorption channels, each having a distinct energy content (e.g., translational temperatures of 2700, 900 and 150 K). Through control studies, in which molecular CO was adsorbed on the surface, the most energetic CO channel is the result of CO photodesorbing from defect sites on the surface. This channel was found to be absent when the  $\text{Mo}(\text{CO})_6$  adsorption was performed with the surface temperature held at 160 K, where the molecular CO will not bind to the substrate. While defects have been thought to play an important role in certain thermal reactions, the present measurements have provided the first compelling evidence of their role in nonthermal reactions. The two remaining CO channels result from  $\text{Mo}(\text{CO})_6$  photodecomposition. The internal state and translational energy distributions of the CO species for these two channels are quite distinct, and are consistent with the model proposed previously: the energetic CO channel results from CO photoproducts that are directly ejected into the gas phase with little interaction with the substrate/adlayer, while the remaining channel, which has an energy content that is nearly equilibrated with the surface, is the result of CO species that have undergone extensive interactions with the substrate/adlayer. By comparing measured cross sections and energy disposal in the CO fragments by the photodecomposition of isolated, gas phase  $\text{Mo}(\text{CO})_6$  it is apparent that there is significant excited state energy quenching. The coverage dependence of the cross section for the photodecomposition of  $\text{Mo}(\text{CO})_6/\text{Si}(111)$  reveals a step-like factor of three increase at the completion of approximately one monolayer. There is, however, no corresponding variation in the CO energy disposal, which is found to be independent of  $\text{Mo}(\text{CO})_6$  coverage. Previous NIST work had shown that completion of the monolayer corresponds to coalescing of two dimensional  $\text{Mo}(\text{CO})_6$  islands and the subsequent onset of multilayer growth, so the lack of any change in the energy partitioning takes on special significance. These new data suggest that quenching by the substrate is not the result of energy relaxation, but rather is due to quantum efficiency and/or absorption effects. This conclusion brings into question the widely held view that changes in quantum efficiency and absorption effects will be secondary effects compared to changes in energy damping at surfaces.



## 20. Substitution Induced Mid-Gap States in Mixed-Metal Titanates

**S.W. Robey, L.T. Hudson, R.V. Smilgys, C. Eylem (U. Md - Center for Superconductivity Research), and B. Eichorn (U. Md - Center for Superconductivity Research)**

Transition metal oxides are candidate materials in a wide range of technologies. Possible applications range from the use of high transition temperature superconductors in microwave components and superconducting electronics to ferroelectric materials for modulators, second harmonic generation media, and waveguides in optoelectronic technologies. We are performing studies of the electronic structure of novel oxides as part of a comprehensive collaborative program with the Center for Superconductivity Research at the University of Maryland to develop new materials. Another goal of the research is to determine the important physical processes involved in doped metal oxide systems and how these influence desired material properties. A variety of oxide systems have been synthesized at the University of Maryland and structural, transport, and magnetic properties characterized. Synchrotron radiation supplied by the NIST SURF II storage ring is used in photoelectron spectroscopy studies of the electronic structure. This allows us to link information on the material properties with detailed characterization of the electronic states involved in determining these properties. Research over the past year has concentrated on studies of rare earth substituted titanate systems which form solid solutions over a wide range of compositions, leading, in turn, to a wide variety of material properties from semiconductors to metals to highly correlated Mott-Hubbard insulators. Photoelectron spectroscopy studies have provided clues to the nature of the transitions between these different phases, and consequently, the greatly varying transport and magnetic properties. For instance, we have observed spectral detail that provides information of the opening of the Mott-Hubbard gap in correlated materials as the material is doped.

As another part of this research program we are employing photoelectron spectroscopy and other surface sensitive techniques to study surface/interface problems associated with developing thin film applications of these novel oxides. Work over the past year has concentrated on Reflection High Energy Electron Diffraction (RHEED) studies of the surface quality and processing of substrate materials necessary for growth of these oxides in thin film form.

## 21. Magnetic Thin Films

**W.F. Egelhoff, Jr., M.T. Kief, D. Lewis (Physical Science Trainee), Y. Kadmon (Negev Nuclear Research Center, Israel), and M.D. Stiles**

The Magnetic Thin Films program consists of an experimental effort and a related theoretical effort.

- (a) Magnetic Engineering Competence (Egelhoff, Kief, Lewis, Kadmon): The objective of the experimental project is to provide assistance in manufacturing process engineering to those US companies in the magnetic data-storage industry that have received ATP grants. In recent years, new classes of magnetic thin films have been discovered that have great potential as commercial products. Two such products are a new generation of magnetic recording heads that can read ultra-high-density (10 Gbits/in<sup>2</sup>) data stored on hard discs and a new generation of nonvolatile memory chips. Both products are based on the "giant magnetoresistance effect" which is found in certain types of magnetic thin films. We have begun studying the details of the manufacturing process for such products in collaboration with two ATP-grant recipients, Nonvolatile Electronics, Inc. and the National Storage Industry Consortium (which includes Hewlett Packard, IBM, Digital, Read-Rite, Quantum, and Applied Magnetics).

We have almost completed installation of the new Magnetic Engineering Research Facility which is 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 seven magnetron sputter-deposition guns, a complete molecular beam epitaxy system with Knudsen cells and electron-beam evaporators, a variety of film-thickness monitors, a scanning tunneling microscope (STM), ion scattering spectroscopy, reflection high-energy electron diffraction, spot-profile-analysis low-energy electron diffraction, Auger-electron and x-ray photoelectron spectroscopies (XPS), and an electromagnet and a superconducting magnet that are equipped for measuring the magnetoresistance and magneto-optical properties such as Kerr rotation and ellipticity (including spectroscopic Kerr and spectroscopic ellipsometry measurements). A sample interlock and transport mechanism permits in-vacuum access to all parts of the facility. In our initial studies of films manufactured by Nonvolatile Electronics, Inc., we found, using XPS and the STM, an unexpected granular character to the films that disrupts the desired layer-by-layer structure which is expected to exhibit the best device performance. We are presently investigating modifications to the manufacturing process which we believe may correct this problem and move these prototype films one step closer to commercialization.

- (b) Theory of Exchange Coupling in Magnetic Thin Films (Stiles): The objective of this theoretical project is to understand the antiferromagnetic coupling between magnetic thin films separated by non-magnetic spacer layers. In devices based on the giant magnetoresistance effect, this coupling determines the field required to reverse the magnetization; the weaker the coupling, the more sensitive is the device as a detector of magnetic fields. In measurements of the coupling as a function of spacer layer thickness, the coupling oscillates between ferromagnetic and antiferromagnetic. To test whether these oscillations originate from Fermi-surface properties of the spacer-layer material, calculations have been made of the Fermi surfaces for a set of 18 spacer materials. Periods measured in samples with spacer layers made of noble metals, which have very

simple Fermi surfaces, agree with those calculated from the Fermi-surface properties. For transition-metal spacer layers, which have very complicated Fermi surfaces, the measured periods are consistent with the Fermi-surface properties although many more periods are found in the calculation than are found experimentally. Confirmation that the oscillations originate from Fermi-surface properties requires calculation of the coupling strength in addition to the periodicities. This calculation is in progress.

## 22. Grazing-Angle X-Ray Photoemission Spectroscopy of Semiconductor Oxides

**T. Jach and M.J. Chester**

The analysis and control of oxide layers on semiconductor surfaces is one of the most important issues in device fabrication. Currently, there is no suitable technique for simultaneous identification of the oxide species, the depth distribution of each species, and the oxide densities for oxide layers in the relevant thickness range of 1-4 nm. We have utilized x-ray photoemission spectroscopy at grazing incidence and x-ray reflectance measurements to obtain quantitative data on all of the above-mentioned quantities. The measuring apparatus, which was the subject of a recently-awarded US Patent, makes use of the near-total reflection of x-rays from the oxide surface at different grazing-incidence angles to vary the x-ray penetration depth. X-ray photoelectron spectra taken at the different incidence angles are analyzed to determine the depth distributions of different chemical species near the surface in a non-destructive manner. The x-ray reflectance data give information on surface roughness and oxide-layer thickness. Measurements have been made for oxide surfaces on gallium arsenide, germanium, and silicon. We have observed oxide layers on gallium arsenide surfaces which allow us to reject certain models of oxidation. An unexpected oxide species has been found on the germanium surface. Finally, we have made thickness and density measurements on silicon surfaces that have been oxidized in different ways.

## 23. Improved Surface Analyses by Auger-Electron Spectroscopy and X-Ray Photoelectron Spectroscopy

**C.J. Powell**

Auger-electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) are the two techniques most commonly used for practical surface analyses. The accuracies of AES and XPS analyses, however, are poor in comparison with bulk analytical techniques on account of many sources of significant systematic error. In a collaboration with Prof. A. Jablonski (Polish Academy of Sciences), an evaluation has been completed of the complicating effects of elastic electron scattering in the formalism for AES and XPS analyses. A surprising result of this evaluation was that the relatively simple formalism in common use (developed from a model in which elastic scattering is neglected) can still be used for analyses of homogeneous materials but

only if the electron inelastic mean free path (IMFP) is used in the application rather than the conventional electron attenuation length (AL). In other collaborative work with Drs. D. R. Penn (Electron and Optical Physics Division, Physics Laboratory) and S. Tanuma (Nippon Mining Company, Japan), new calculations have been completed of electron IMFPs for a group of fourteen organic compounds. This new set of IMFPs has been analyzed with earlier sets of IMFP data for groups of elements and inorganic compounds to yield a predictive IMFP formula that is expected to be valid for all materials. The new formula is based on a sound physical model and is about three times more accurate than an empirical AL formula in common use. Finally, the biennial Topical Conference on Quantitative Surface Analysis has been organized to disseminate information on recent advances that will further improve the accuracy of AES and XPS analyses.

#### **24. Collisional Electron Transfer Mechanisms at Ion-Bombarded Surfaces**

**J. Fine, K. Franzreb (Univ. of Kaiserslautern, Germany), and M. Yoshitake (National Research Institute for Metals, Japan)**

Our understanding of ion-bombardment-activated surface chemistry and radiation-damage mechanisms in compound materials has advanced considerably this year. We had previously identified a new class of ion-induced collisional processes in alkali halides that are characterized by a sequence of inelastic collisions involving localized electron transfer and valence change. This electron-transfer collision process has been further investigated in new measurements of ion-induced Auger-electron spectra of other inorganic compounds in a continuing collaboration with Prof. M. Szymonski, Jagellonian University, Krakow. A systematic study of the role of the collision partner and its valence state on the electron-transfer process has resulted in a new model for the process energetics. According to this model, specific energy levels of the system are perturbed during the collision and it is these levels that control the probability for electron transfer. The electron-transfer probabilities depend strongly on the binding energies and valence state of the collision partners, and are strongly enhanced when certain energy levels cross or are near-resonant. We have identified the levels involved in this Landau-Zener-type of level-crossing and have shown that our model is consistent with the measurements. Our model can thus be used to predict the occurrence of electron-transfer processes in ion-initiated collisions and then used to predict the stability or reactivity of bombarded compounds. What is remarkable about this class of collisional processes is that the collisions can initiate electronic processes which are similar to those stimulated by energetic electrons or x-rays. It seems that this collisional electron-transfer process may be the ion-bombardment analog of the well-known Knotek-Feibelman mechanism initiated by electron or x-ray radiation.

## 25. Hot Electrons and Surface Femtochemistry

**J.W. Gadzuk**

An exciting new area of ultra-fast, photon-induced molecular processes at surfaces, referred to as surface femtochemistry, could have potential applications within a broad range of delicate surface fabrication processes. The new hot-electron surface femtochemistry is based on a mechanism in which ultraviolet laser light is directed onto a surface or interface upon which a chemical bond-making or -breaking reaction is to occur. The surface can serve as either an electron source, a momentum source, an antenna for incident radiation, or an entity in the "large" molecule undergoing the 'femtochemical' transition. According to our theoretical modeling, photon absorption by valence-electron excitation of the substrate is followed by a cascade process that creates hot electrons, which in turn undergo ultrafast reactive charge-transfer scattering at the surface. The highly non-equilibrium distribution of products forms rapidly compared to the timescales required for thermal chemistry, and it is for this reason that hot-electron surface femtochemistry is so promising for applications in which the chemical system would not survive changes induced by thermal processing. The present theory demonstrates how localized energy from the inelastic scattering event can be used to stimulate elementary surface femtochemical processes such as vibrational or rotational excitation, surface dissociation, and dissociative or unreactive desorption. Selective control of the quantum-state-specific product branching ratios can be attained from the theoretical guidelines by tailoring the incident hot-electron distribution both through temporal shaping of the laser pulse and through proper choice of the photon energy in relation to the electronic excitation spectrum of the substrate and the surface molecule.

C. **Outputs and Interactions**  
(Surface and Microanalysis Science Division)

1. **Publications**

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## 2. Talks

Bennett, J., "Ultrashallow Depth Profiling with Time-of-Flight Secondary Ion Mass Spectrometry," 2nd International Workshop on the Measurement and Characterization of Ultrashallow Doping Profiles in Semiconductors, Research Triangle Park, NC, March 23, 1993.

Bennett, J., "Secondary Ion Images from Semiconductor Surfaces Modified by Scanning Tunneling Microscopy," 6th East Coast Workshop on SIMS, Hopewell Junction, NY, May 20, 1993.

Bennett, J., "Report from the International Workshop on the Measurement and Characterization of Ultrashallow Doping Profiles in Semiconductors," 6th East Coast Workshop on SIMS, Hopewell Junction, NY, May 21, 1993.

Bright, D.S., "Architecture/Environments for Image Processing - Hardware and Software for the Microscopist," Microscopy Society of America 51st Annual Meeting, Cincinnati, OH, August 4, 1993. Invited

Bright, D.S., "Image Processing and Free Software for the Microscopist," Metropolitan Microscopy Society, Paramus, NJ, March 31, 1993. Invited

Buntin, S., "Photodecomposition Dynamics of Mo(CO)<sub>6</sub>Si(111)," European Science Foundation Workshop on Photoinduced Processes at the Gas-Solid Interface, Fritz-Haber-Institute, Berlin, Germany, October 19, 1992. Invited

Cavanagh, R.R., "Time-Resolved Studies of Vibrational Relaxation: Model Compounds to Molecules on Surfaces," Chemistry Department, Wayne State University, Detroit, MI, October 7, 1992. Invited

Cavanagh, R.R., "Time-Resolved Probes of Adsorbate-Substrate Energy Transfer," High Resolution Spectroscopy Conference, Salt Lake City, UT, January 20, 1993.

Cavanagh, R.R., "Laser Probes of Energy Transfer at Surfaces," Gordon Research Conference on Chemical Reactions at Surfaces, Ventura, CA, March 9, 1993.

Cavanagh, R.R., "Time-Resolved Measurements of Substrate to Adsorbate Energy Transfer," Faraday General Discussion 96 Dynamics at the Gas-Solid Interface, Cambridge, England, September 14, 1993. Invited



- Chester, M.J., "A Few Notes on Surface Physics," Department of Physics, Mansfield State College, Mansfield, PA, February 11, 1993. Invited
- Chester, M.J., "Grazing Incidence X-Ray Photoemission Study of Oxidized GaAs(100)," American Physical Society Meeting, Seattle, WA, March 24, 1993.
- Chi, P.H., "Thermal Stability Study of Titanium in AlInAs and InP by Secondary Ion Mass Spectrometry," Sixth East Coast Workshop on Secondary Ion Mass Spectrometry, IBM Corporation, East Fishkill Facility, Hopewell Junction, NY, May 20, 1993.
- Chu, P.M., "State-Resolved Photofragmentation Dynamics of Mo(CO)<sub>6</sub>/Si(111)," American Vacuum Society Meeting, Chicago, IL, November 10, 1992.
- Chu, P.M., "Photodissociation Dynamics of Mo(CO)<sub>6</sub>/Si(111): Localized Adsorbate Excitation," Chemistry Department Seminar, Notre Dame University, Notre Dame, IN, January 11, 1993. Invited
- Chu, P.M., "Photodissociation Dynamics of Mo(CO)<sub>6</sub>/Si(111): Localized Adsorbate Excitation," Chemistry Department Seminar, Mount Holyoke College, South Hadley, MA, February 1, 1993. Invited
- Conny, J.M., "Modeling the Isotopic Composition of Atmospheric CO," Amer. Geo. Union 1993 Spring Meeting, Baltimore, MD, May 25, 1993.
- Currie, L.A., "On the Synergism between Statistics and Chemistry," American Statistical Association, Philadelphia, PA, October 9, 1992. Invited
- Currie, L.A., "Exploratory Data Analysis of QA Program Trends," NIST/NCI QA Micronutrient Analysis Workshop, Rockville, MD, November 14, 1992. Invited
- Currie, L.A., "Data Exploration," Patrick Air Force Base, FL, December 9, 1992. Invited
- Currie, L.A., "Total Quality Aspects of SRM Selection/Production," Panelist at the Workshop on Standard Reference Materials, National Physical Laboratory, New Delhi, February 6, 1993. Invited
- Currie, L.A., "Accuracy in Measurement, Detection, and Reporting of Trace Element Data: An International Perspective," 4th International Conference on the Health and Disease: Effects of Essential Toxic Trace Elements, New Delhi, India, February 11, 1993. Invited

- Currie, L.A., "Total Quality Measurement in Multivariate Studies of Trace Elements in Air Pollution and in Dietary Intake," Indira Gandhi Centre for Atomic Research, Kalpakkam, India, February 15, 1993. Invited
- Currie, L.A., "Fundamentals of Accelerator Mass Spectrometry and its Application to Environmental Studies," Indira Gandhi Atomic Research Centre for Atomic Research, Kalpakkam, India, February 17, 1993. Invited
- Currie, L.A., "Introduction Remarks: Environment," Conf. on Extreme Value Theory and its Applications, Environment Session, NIST, Gaithersburg, May 7, 1993. Invited
- Currie, L.A., "Overview of the International Chemical Community's Approach to Detection Limits," ISO/IUPAC Meeting on Nomenclature Related to Limits of Detection, Washington, D.C., July 21, 1993. Invited
- Currie, L.A., "Statistical and Chemical Issues in Detection and Environmental Modeling," Gordon Conference on Statistics in Chemistry and Chemical Engineering, New Hampton, NH, July 26, 1993. Invited
- Currie, L.A. and Spiegelman, C.S., "Statistical and Chemical Aspects of Detection," 2nd Conference on Statistics, Earth and Space Sciences (CHESM), Bologna, Italy, August 22, 1993. Invited
- Currie, L.A., "Isotopic Measurements and Standards for Tropospheric Gases and Particles," 6th International Conference on Accelerator Mass Spectrometry, Workshop No. 1, Institute of Geological and Nuclear Sciences, Lower Hutt, New Zealand, September 23, 1993. Invited
- Currie, L.A., "Optimal Estimation of Uncertainty Intervals for Accelerator and Decay Counting," 6th International Conference on Accelerator Mass Spectrometry, Australian National University, Canberra, Australia, September 28, 1993. Invited
- Currie, L.A., "Fossil-and Bio-Mass Combustion: C-14 for Source Identification, Chemical Tracer Development, and Model Validation," 6th International Conference on Accelerator Mass Spectrometry, University of Sydney, Sydney, Australia, September 30, 1993. Invited
- Egelhoff, Jr., W.F., "A SPA-LEED Study of the Epitaxial Growth of Fe, Co, and Cu on Cu(100) at 80K-300K," American Vacuum Society Meeting, Chicago, IL, November 13, 1992.
- Egelhoff, Jr., W.F., "A SPA-LEED Study of Fe, Co, and Cu Films on Cu(100)," Materials Research Society Meeting, San Francisco, CA, April 15, 1993.

- Egelhoff, Jr., W.F., "A Study of the Structure and Magnetic Properties of Epitaxial Fe Films on Cu(100)," Materials Research Society Meeting, San Francisco, CA, April 15, 1993.
- Egelhoff, Jr., W.F., "The New NIST Magnetic Engineering Facility and Opportunities for Collaborative Research," Workshop on Magnetic Information Storage Technology, Monterey, CA, June 2, 1993. Invited
- Etz, E.S., "The Raman Spectrum of CVD Diamond as a Measure of Diamond Quality and Performance," Second NIST Workshop on Characterizing Diamond Films, NIST, February 25, 1993.
- Fine, J., "New Collisional Deexcitation Processes at Ion Bombarded Surfaces," Argonne National Laboratory, Chicago, IL, November 6, 1992. Invited
- Fine, J., "Electron Stimulated Desorption Mechanisms in Insulators," American Vacuum Society Meeting, Chicago, IL, November 11, 1992.
- Fine, J., "VAMAS Report on the Evaluation of LOGIT for the Measurement of Interface Widths," ASTM/American Vacuum Society Meeting, Chicago, IL, November 12, 1992. Invited
- Fine, J., "Topographic and Mass Transport Dependent Broadening Process at Interfaces," ASTM/American Vacuum Society Meeting, Chicago, IL, November 13, 1992. Invited
- Fine, J., "Collisional Deexcitation Mechanisms at Ion-Bombarded Sodium Halide Surfaces," International Workshop on Electronic Excitations at Surfaces on Halides, Krakow-Przegorzaly, Poland, May 4, 1993. Invited
- Fine, J., "Sequential Electron Capture Collisions in Sodium Halides," Symposium on Surface Science, Kaprun, Austria, May 12, 1993.
- Fine, J., "Interface Broadening Processes Associated with Sputter-Depth-Profile Analysis," Jagellonian University, Krakow, Poland, May 19, 1993. Invited
- Fine, J., "Basic Radiation Damage Processes in Ionic Solids: The Role of Collisional Electron Capture," Molecular Science Research Center, Pacific Northwest Laboratories, Richland, WA, July 13, 1993. Invited
- Fletcher, R.A., Small, J.A., and Blackburn, D.H., "Analysis of Atmospheric and Carbon Airborne Particles Collected Behind a High Temperature Heated Inlet," Eleventh Annual Meeting of The American Association for Aerosol Research, San Francisco, CA, Oct. 13, 1992.

- Franzreb, K., "Sputtering of Silver and Copper Molecules," Argonne National Laboratory, Chicago, IL, September 14, 1993.
- Franzreb, K., "Electron Emission From Ion-Bombarded Ionic Compound Surfaces," University of Kaiserslautern, Kaiserslautern, Germany, April 30, 1993.
- Franzreb, K., "Electron Emission from Ion-Bombarded Ionic Compound Surfaces," Workshop on Electronic Excitations at Surfaces of Halides, Jagellonian University, Krakow, Poland, May 5, 1993.
- Gadzuk, J.W., "Hot Electrons Cascades in Surface Photochemistry," Workshop on Photoinduced Processes at the Gas-Solid Interface, Fritz-Haber-Institute, Berlin, Germany, October 19, 1992. Invited
- Gadzuk, J.W., "Inelastic Resonance Scattering, Tunneling, and Desorption," Institute Colloquium, Fritz-Haber-Institute, Berlin, Germany, October 22, 1992. Invited
- Gadzuk, J.W., "Russell Young: His Contributions to Proximal Probes," American Vacuum Society Meeting, Chicago, IL, November 10, 1992. Invited
- Gadzuk, J.W., "Inelastic Resonance Scattering, Tunneling and Desorption," Condensed Matter Seminar, University of Maryland, College Park, MD, February 11, 1993. Invited
- Gadzuk, J.W., "The Key to Surface Femtochemistry," Femtosecond Chemistry--The Berlin Conference, Freie Universität, Berlin, Germany, March 3, 1993. Invited.
- Gadzuk, J.W., "Single Atom Point Source for Electrons: Field Emission Resonance Tunneling Revised in an STM World," Physics Department, Fritz Haber Institut, Berlin, Germany, March 4, 1993. Invited.
- Gadzuk, J.W., "Hot Electron Cascades in Laser-Excited Surface Photochemistry," American Physical Society Meeting, Seattle, WA, March 23, 1993.
- Gadzuk, J.W., "R-Matrix Approach to Resonant Tunneling," American Physical Society Meeting, Seattle, WA, March 24, 1993.
- Gadzuk, J.W., "Vibronic Excitation in Resonant Molecular Surface Half Collisions," Vibronic Processes in Gas Phase and Surface Scattering Workshop, Pousada de Palmela, Portugal, May 10, 1993. Invited
- Gadzuk, J.W., "Overview of Surface Science," Second European Science Foundation Summer School in Surface Science, Hindas, Sweden, August 15, 1993. Invited

- Gadzuk, J.W., "Fundamentals of Femtochemistry at Surfaces," Second European Science Foundation Summer School in Surface Science, Hinda, Sweden, August 17, 1993. Invited
- Germer, T., "Time-Resolved Measurement of Surface to Adsorbate Energy Transfer," American Vacuum Society Meeting, Chicago, IL, November 12, 1992.
- Germer, T., "Ultrafast Transient Infrared Absorption Measurements of Surface to Adsorbate Energy Transfer: Electronic vs. Phonon Effects," Quantum Electronics and Laser Science Conference, Baltimore, MD, May 5, 1993. Invited
- Germer, T., "Time-Resolved Measurements of Energy Transfer at Metal Surfaces," Physics Department Seminar, Utah State University, Logan, UT, June 1, 1993. Invited.
- Gillen, J.G., "Application of Secondary Ion Mass Spectrometry for Elemental and Molecular Microanalysis of Biological Materials," 32nd ORNL-DoE Conf. on Analytical Chemistry, Gatlinburg, TN, October 7, 1992.
- Gillen, J.G., "Molecular Ion Imaging of Patterned Self Assembled Monolayers by SIMS," Sixth East Coast Workshop on Secondary Ion Mass Spectrometry, IBM Corporation, East Fishkill Facility, Hopewell Junction, NY, May 20, 1993.
- Gillen, J.G., "High Spatial Resolution Isotope Ratio Imaging Using Secondary Ion Mass Spectrometry," Proceedings of the 41st ASMS Conference on Mass Spectrometry and Allied Topics, San Francisco, CA, May 30-June 4, 1993.
- Jach, T., "Grazing Incidence Photoemission: A New Way to Obtain Depth Analysis in Semiconductor Oxides," American Physical Society Meeting, Seattle, WA, March 24, 1993.
- Jach, T., "Diffraction Studies of Epitaxially Grown Dilute Magnetic Semiconductors," High Energy Synchrotron Source User's Meeting, Cornell University, Ithaca, NY, June 22, 1993.
- Jach, T., "Depth Studies of Semiconductor Oxides by Grazing Incidence X-Ray Photoemission Spectroscopy," Gordon Research Conference on X-Ray Physics, New London, NH, August 10, 1993.
- Kief, M., "Investigation of Perpendicular Magnetic Surface Anisotropy for Ultrathin Films of Fe and Co on Cu(100), Cu(111), and Cu(110)," 37th Annual Conference on Magnetism and Magnetic Materials, Houston, TX, December 3, 1992.

- Kief, M., "Structure and Growth Kinetics of Metastable Metal Films on Single-Crystal Metal Substrates," Materials Research Society Meeting, San Francisco, CA, April 13, 1993.
- Klinedinst, D.B., "Radiocarbon Measurements of Extractable Organic Matter from the Integrated Air Cancer Project Study in Roanoke, VA," Measurement of Toxic and Related Air Pollutants 1993 AWMA International Symposium, Durham, NC, May 4, 1993.
- Klinedinst, D.B. and Currie, L.A., "Comparative Study of Fe-C Bead vs. Graphite Target Performance with the NOSAMS Facility Recombinator Ion Source," 6th International Conferences on Accelerator Mass Spectrometry, Canberra, Australia, September 28, 1993. Invited
- Klouda, G.A., "Tropospheric Ozone Precursors: Tracking Down the Sources of Volatile Organic Carbon via Isotope ( $^{14}\text{C}$ ) Measurements," Measurement of Toxic and Related Air Pollutants, 1993 AWMA International Symposium, Durham, NC, May 3-7, 1993.
- Klouda, G.A., "Tropospheric Ozone Precursors: Tracking Down the Sources of Volatile Organic Carbon via Isotope ( $^{14}\text{C}$ ) Measurements," Southern Oxidants Study Data Analysis Workshop, Denver, CO, May 12, 1993.
- Klouda, G.A., "Radiocarbon Measurements of Urban Tropospheric Carbon Monoxide: Use of a Factorial Design Sampling Strategy," presented at the Spring 1993 Meeting of the American Geophysical Union, Baltimore, MD, May 24-28, 1993.
- Klouda, G.A., "Source Identification of Atmospheric Carbonaceous Aerosols and Gases via Radiocarbon Measurements: Applications to Urban Air Quality," presented to the Energy, Resource and Environmental Systems Division, The MITRE Corporation, McLean, VA, August 18, 1993. Invited
- Marinenko, R.B., "Elemental Compositional Mapping with the Electron Probe Microanalysis," Department of Chemistry Seminar, Drexel University, Philadelphia, PA, November 11, 1992.
- Marinenko, R.B., "Has Automation Taken the Worry Out of Quantitative Wavelength Dispersive Analysis?" 28th Conference of the Microbeam Analysis Society, Loyola Marymount University, Monrovia, CA, July 14, 1993.
- Myklebust, R.L., "Fitting Wavelength Dispersive Spectra in the NIST/NIH DTSA Program," 1993 Microbeam Analysis Meeting, Loyola Marymount University, Los Angeles, CA, July 16, 1993.

- Newbury, D.E., "Trace Nanoanalysis: Achieving High Sensitivity and High Spatial Resolution," E.I. Dupont Corporation Experimental Station, Wilmington, DE, December 8, 1992.
- Newbury, D.E., "Trace Nanoanalysis: Achieving High Sensitivity and High Spatial Resolution," Metropolitan Microbeam Analysis Society, Paramus, NJ, December 9, 1992. Invited
- Newbury, D.E., "Trace Nanoanalysis: Achieving High Sensitivity and High Spatial Resolution," AT&T Bell Laboratories, Murray Hill, NJ, December 10, 1992. Invited
- Newbury, D.E., "Trace Nanoanalysis: Achieving High Sensitivity and High Spatial Resolution," Dept. of Chemistry, Physical/Analytical Chemistry Seminar, University of Maryland, College Park, MD, January 27, 1993. Invited
- Newbury, D.E., "Trace Element Imaging by Secondary Ion Mass Spectrometry: Seeking the Limits," 1993 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Georgia World Congress Center, Atlanta, GA, March 8, 1993. Invited
- Newbury, D.E., "Basic Concepts of X-ray Microanalysis," Southeast Electron Microscope Society Spring Conference, Birmingham, AL, April 12, 1993. Invited
- Newbury, D.E., "Quantitative Compositional Mapping with the Electron Probe Microanalyzer," Scanning 93 Conference, Orlando, FL, April 22, 1993. Invited
- Newbury, D.E., "The Contributions of Ludwig Reimer to the Simulation of Electron Beam-Specimen Interactions," Scanning 93 Conference, Orlando, FL, April 22, 1993. Invited
- Newbury, D.E., "Simulating Electron-Excited Energy Dispersive X-ray Spectra with NIST Desktop Spectrum Analyzer," Scanning 93 Conference, Orlando, FL, April 23, 1993. Invited
- Newbury, D.E., "Trace Nanoanalysis: Achieving High Sensitivity and High Spatial Resolution," Southeast Electron Microscope Society Spring Conference, Birmingham, AL, May 12, 1993. Invited
- Newbury, D.E., "Artifacts in Energy Dispersive X-ray Spectrometry - Are Things Getting Any Better?," 27th Annual Conference of the Microbeam Analysis Society, Loyola Marymount University, Los Angeles, CA, July 11, 1993. Invited
- Newbury, D.E., "Microanalysis from the Other Side - Relating Microscopic Measurements to Bulk Analysis," 27th Annual Conference of the Microbeam Analysis Society, Loyola Marymount University, Los Angeles, CA, July 11, 1993. Invited

- Newbury, D.E., "Trace Nanoanalysis of Nanophase Magnetic Ceramics by Analytical Electron Microscopy with Parallel Detection Electron Energy Loss Spectrometry," 27th Annual Conference of the Microbeam Analysis Society, Loyola Marymount University, Los Angeles, CA, July 11, 1993.
- Newbury, D.E., "Basic Literacy in Electron-Excited Energy Dispersive X-ray Microanalysis," 51st Conference of the Microscopy Society of America, Cincinnati, OH, August 2, 1993. Invited
- Newbury, D.E., "Ion Microscope and Microprobe Studies of Surfaces and Interfaces," 51st Conference of the Microscopy Society of America, Cincinnati, OH, August 3, 1993. Invited
- Newbury, D.E., "Detection Limits for Analytical Electron Microscopy with Electron Energy Loss Spectrometry and Energy Dispersive X-ray Spectrometry," 51st Conference of the Microscopy Society of America, Cincinnati, OH, August 5, 1993. Invited
- Newbury, D.E., "Exploring the Microstructure of Matter with Modern Microscopy," Art Department, Degenstein Theatre and Art Gallery, Susquehanna University, Selinsgrove, PA, September 8, 1993. Invited
- Powell, C.J., "Comparison of Formulae for Electron Inelastic Mean Free Paths and Attenuation Lengths," Twelfth International Vacuum Congress and Eighth International Conference on Solid Surfaces, The Hague, The Netherlands, October 13, 1992.
- Powell, C.J., "Activities of ISO Technical Committee 201 on Surface Chemical Analysis," ASTM/American Vacuum Society Meeting, Chicago, IL, November 10, 1992. Invited
- Powell, C.J., "The NIST X-Ray Photoelectron Spectroscopy Database," American Vacuum Society Meeting, Chicago, IL, November 12, 1992.
- Powell, C.J., "Formalism and Parameters for Quantitative Surface Analysis by Auger-Electron Spectroscopy and X-Ray Photoelectron Spectroscopy," Symposium on Applied Surface Analysis, Case Western Reserve University, Cleveland, OH, June 9, 1993.
- Powell, C.J., "The Role of Matrix Factors in Quantitative AES and XPS," Research Center for Surface and Vacuum Investigations, Gosstandart, Russia, July 21, 1993. Invited
- Powell, C.J., "Effects of Elastic and Inelastic Electron Scattering on Quantitative Surface Analyses by AES and XPS," Fifth International Conference on Electron Spectroscopy, Kiev, Ukraine, July 27, 1993. Invited



- Richter, L.J., "State-Resolved Studies of Surface Photoreactions," Radiation Laboratory Seminar, Columbia University, New York, NY, October 26, 1992. Invited
- Richter, L.J., "State-Resolved Studies of Surface Photoreactions," University of Chicago, Chicago, IL, November 6, 1992. Invited
- Robey, S.W., "Mixed Oxides Formed by Substitution of Y, La, and Nd for Ba in BaTiO<sub>3</sub>: The Characteristics of Mid-Gap States," Physics and Chemistry of Molecular and Oxide Superconductors Conference, Eugene, OR, July 28, 1993.
- Robey, S.W., "Electronic Structure of BaTiO<sub>3</sub> and R<sub>0.33</sub>Ba<sub>0.67</sub>TiO<sub>3,δ</sub>, where R=Y, La, and Nd," Eighth International Meeting on Ferroelectricity, NIST, Gaithersburg, MD, August 12, 1993.
- Simons, D.S., "Assessment of Silicon Wafer Cleaning Procedures by Secondary Ion Mass Spectrometry," Sixth East Coast Workshop on Secondary Ion Mass Spectrometry, IBM Corporation, East Fishkill Facility, Hopewell Junction, NY, May 20, 1993.
- Simons, D.S., "Assessment of Silicon Wafer Cleaning Procedures by Secondary Ion Mass Spectrometry," Microbeam Analysis Society, Los Angeles, CA, July 12, 1993.
- Simons, D.S., "Quantification in SIMS - Some Success Stories," Ninth International Conference on Secondary Ion Mass Spectrometry, Yokohama, Japan, November 10, 1992. Invited
- Small, J.A., "Automated Electron Probe Analysis of Particulate Populations," Eleventh Annual Meeting of AAAR, San Francisco, CA, October 14, 1992.
- Small, J.A., "An Evaluation of Particle Correction Procedures Applied to Automated Particle Analysis," Microbeam Analysis Society Annual Meeting, Los Angeles, CA, July 15, 1993.
- Small, J.A., "Current Trends in Microbeam Analysis in the U.S.A.," European Microbeam Analysis Society, Rimini, Italy, May 10, 1993.
- Smilgys, R.V., "Influence of Substrate Preparation on the Growth of DyBaCuO Thin Films on MgO," American Vacuum Society Meeting, Chicago, IL, November 10, 1992.
- Steel, E.B., "Characterization of Particles: Microanalysis," Environmental Protection Agency, Research Triangle Park, NC, March 5, 1993.
- Steel, E.B., "Status of Proficiency Testing and Asbestos Methods," Environmental Information Association, Nashville, TN, April 5, 1993.

- Steel, E.B., "Proficiency Testing: Polarized Light and Transmission Electron Microscopic Analysis of Asbestos," Eastern NVLAP Regional Meeting, Atlanta, GA, June 22, 1993.
- Steel, E.B., "Proficiency Testing: Polarized Light and Transmission Electron Microscopic Analysis of Asbestos," Mid-Western NVLAP Regional Meeting, St. Louis, MO, July 28, 1993.
- Steel, E.B., "Proficiency Testing: Polarized Light and Transmission Electron Microscopic Analysis of Asbestos," Western NVLAP Regional Meeting, San Francisco, CA, August 25, 1993.
- Stiles, M.D., "Fermi Surface Effects in Magnetically Coupled Layers," 37th Annual Conference on Magnetism and Magnetic Materials, Houston, TX, December 2, 1992. Invited.
- Stiles, M.D., "BEEM: A Status Report," Ballistic Electron Emission Microscopy Workshop, Williamsburg, VA, January 25, 1993. Invited
- Stiles, M.D., "Theoretical Aspects of BEEM," Gordon Research Conference on Scanning Tunneling Microscopy, Ventura, CA, March 19, 1993. Invited
- Stiles, M.D., "Oscillatory Magnetic Coupling in Metallic Heterostructures," American Physical Society Meeting, Seattle, WA, March 23, 1993.
- Velapoldi, R.A., "Research at a Government Laboratory: NIST," University of Virginia, Charlottesville, VA, November 13, 1992. Invited
- Velapoldi, R.A., "Microprobe Analysis at NIST," DARPA Nuclear Non-Proliferation Sensors Symposium, Patrick Air Force Base, FL, February 10, 1993. Invited
- Velapoldi, R.A., "Source Apportionment and Microanalysis Environmental Samples," EPA/NIST Workshop, Cincinnati, OH, July 14, 1993. Invited
- Wight, S.A., "The Environmental Scanning Electron Microscope and Particle Analysis," Eleventh Annual Meeting of AAAR, San Francisco, CA, October 13, 1992.
- Zeissler, C.J., "VRD Update," DoD Workshop, Pleasanton, CA, June 22, 1993.
- Zeissler, C.J., "VRD Applications," Patrick Air Force Base, FL, October 14, 1993. Invited.

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

Advanced Technology Applications, Inc. (SBIR Phase I Contract Award) C.J. Powell  
ID No. CN-972

Collaborator: HIAC/ROYCO, Dr. Charles Montague (NIST - R.A. Fletcher)

4. Patent Awards and Applications

Myklebust, R.L., Swyt, C.R., and Fiori, C.E., (deceased) "Desktop Spectrum Analyzer and X-ray Database" (Allowed - September 28, 1993)

Jach, T. and Thurgate, S.M., "Grazing Incidence X-Ray Photoemission Spectrometer for Surface and Interface Analysis" (Allowed - July 26, 1993)

5. SRMs

SRM 2135 Ni/Cr Multilayer

SRM 2137 Boron Implant in Silicon Depth Profile Standard

SRM Calibration Dust in Oil for Optical Particle Counters

SRM Aerosol 0.1  $\mu\text{m}$  Concentration Standard

Completed the "Feasibility Study" for the Preparation of Isotopic SRMs for  
Measurements Quality Control for Greenhouse Gases

Central Distributor for the International (IAEA) Isotopically Characterized Natural Gas  
SRMs

6. SRD Activities

SRD 20 X-Ray Photoelectron Spectroscopy Database (Version 2)

SRD Desktop Spectrum Analyzer

Prepared a Database for the Isotopic Characterization of Atmospheric Gases

7. Calibrations

Calibration of Ozone Photometers:

Boeing Company

Compaq Computer Corporation

Environment Canada, AQB

Environment Canada, EPS

Institute of Applied Environmental Research of University of Stockholm (Sweden) - SRP11  
NIST - SRP0  
SRP7 (EPA-RTP)  
Swiss Federal Office of Metrology - SRP14  
Swiss Federal Laboratories for Material Testing and Research - SRP15  
Xerox Corporation  
Volumne Calibration: Gas Analysis Lab., McClellan AFB, CA

## 8. Committee Assignments

### **D.S. Bright**

EMSA/MAS File Standards Committee

### **R.R. Cavanagh**

Gordon Research Conferences - Dynamics of Gas/Surface Interactions ('93) (Vice Chairman)

Laser Surface Interactions Conference, (Co-chair)

Gordon Research Conference on Dynamics at Surfaces (Chair)

### **L.A. Currie**

Advisor for AFIT MS Thesis (Robinson)

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)

Technical Issues Team (DoC-QA) (Leader)

### **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

**J.W. Gadzuk**

International Advisory Committee, 7th International Conference on Vibrations at Surfaces  
CSTL Colloquium Committee  
NIST Information Resource Center (Subject Specialist Consultant)  
CSTL representative to WERB

**G. Gillen**

Ad-hoc panel member of Metallobiochemistry Study Section for NIH panel review of grant proposals  
Voting member of ASTM Committee E-42

**T. Jach**

Organizing Committee for the 8th Annual Conference on Synchrotron Radiation Instrumentation

**G.A. Klouda**

Division 837 Safety Committee

**R.L. Myklebust**

ASTM E-42 Surface Analysis  
ASTM E-42.96 ISO TC/202/TAG on Microbeam Analysis (Chairman)

**D.E. Newbury**

ASTM E-42 Surface Analysis  
NIST Colloquium 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  
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, 13th International Vacuum Congress and 9th International Conference on Solid Surfaces  
Organizing Committee, 5th Topical Conference on Quantitative Surface Analysis (Chairman)  
International Program Committee and Advisory Board, Third International Workshop on Auger Spectroscopy and Electronic Structure

International Scientific Advisory Committee, 6th Conference on Applied Surface  
and Interface Analysis

**L.J. Richter**

Review Panel for Department of Energy's University Instrumentation Program

**S. Robey**

Organizing Committee for the 8th Annual Conference on Synchrotron Radiation  
Instrumentation

**D.S. Simons**

ASTM E-42 Surface Analysis  
ASTM E-42.06 Secondary Ion Mass Spectrometry  
ASTM E-42.09 Standard Reference Material  
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  
ISO/TC 146/SC3/WGI International Standards Organization Committee

**M. Stiles**

4th Workshop on Ballistic Electron Emission Spectroscopy, Program Committee  
Surface Science Lunch Bunch (Organizer)

**R.M. Verkouteren**

CSTL Strategic Planning Committee on the Environment  
CSTL Electronic Notebook Policy Committee

**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**

American Association for Aerosol Research, Instrumental Working Group  
Microbeam Analysis Society, Nomination Committee

**9. Editorships**

**D.S. Bright**

Journal of Computer Assisted Microscopy (Editorial Board)  
Microanalysis Journal (Editor)

**L.A. Currie**

CRC Press Chemometrics Series (Advisory Editor)

**E.S. Etz**

Microbeam Analysis Journal (Editorial Advisory Board)

**J.W. Gadzuk**

Progress in Surface Science (Advisory Editorial Board)

**D.E. Newbury**

Journal of Microscopy (Editorial Review Board)  
Scanning (Editorial Review Board)  
J. Trace and Microprobe Techniques (Editorial Review Board)  
Microbeam Analysis (Editorial Review Board)

**C.J. Powell**

Applications of Surface Science (Editorial Board)  
Surface and Interface Analysis (Editorial Board)  
Methods of Surface Characterization (Editorial Board)  
Journal of Electron Spectroscopy (Editorial Board)  
Surface Science Spectra (Editorial Board)  
Journal of Vacuum Science and Technology A (Associate Editor)

**10. Seminars**

**December 4, 1992**

Robin F. Farrow, IBM Almaden Laboratories, San Jose, CA, "Artificial Layered Magnetic Structures Grown by Molecular Beam Epitaxy." (Division Sponsor: W. F. Egelhoff, Jr.)

**January 25, 1993**

David McIlroy, University of Rhode Island, Kingston, RI, "The Electronic Properties of the Two-Dimensional Surface State Bands of the (1x1)- and (1x2)-phases of Bi/GaSb(110)." (Division Sponsor: T. Jach)

**January 27, 1993**

Michael Van Hove, Lawrence Berkeley Laboratory, Berkeley, CA, "Electron Scattering Techniques for Surface Crystallography." (Division Sponsor: W.F. Egelhoff, Jr.)

**February 11, 1993**

Stuart P. Parkin, IBM Almaden Laboratories, San Jose, CA, "The Giant Magnetoresistance Effect." (Division Sponsor: W.F. Egelhoff, Jr.)

**March 2, 1993**

Janice M. Hicks, Department of Chemistry, Georgetown University, Washington, DC, "A New Nonlinear Optical Circular Dichroism Spectroscopy at Interfaces." (Division Sponsor: L. Richter)

**April 30, 1993**

Mehmet Sarikaya, Department of Materials Science and Engineering, University of Washington, Seattle, WA., "An Introduction to Biomimetics: Materials Design Based on Biological Composites." (Division Sponsor: D.E. Newbury)

**May 13, 1993**

Xiao-xing Xi, Center for Superconductivity Research, University of Maryland, College Park, MD, "Recent Progress in High-T<sub>c</sub> Superconducting Devices." (Division Sponsor: S. Robey)

**June 1, 1993**

Rakhovsky, Vadim I., Center for Surface and Vacuum Investigations, Moscow, Russia, "Methods of Evaluating X-Ray Photoelectron Spectroscopy Data." (Division Sponsor: C.J. Powell)

**June 9, 1993**

James Angell, Air Resources Laboratory, Silver Spring, MD, NOAA, "Atmospheric Trends in Temperature and Ozone." (Division Sponsor: L.A. Currie)

**June 29, 1993**

John Pasik, Solid State and Surface Chemistry Program, Office of Naval Research, Washington, DC, "Research Interests in Solid State and Surface Chemistry at the Office of Naval Research." (Division Sponsor: S. Robey)



**July 6, 1993**

Ian Harrowfield, Electron Microscopy Group, Division of Mineral Products, CSIRO, Port Melbourne, Australia, "The X-ray Continuum - A Resource and a Burden." (Division Sponsor: J.A. Small)

**July 16, 1993**

Paulo Artaxo, Institute of Physics, University of Sao Paulo, Brazil, "Long-Term Ground-Based Monitoring of Biomass Burning Emissions in the Amazon Basin." (Division Sponsor: J.M. Conny)

**July 20, 1993**

Stephen M. Thurgate, Murdoch University, Murdoch, Australia, "New Results in Electron Coincidence Measurements from Solid Surfaces." (Division Sponsor: T. Jach)

**July 30, 1993**

Richard Piner, Physics Department, Appalachian State University, Boone, NC, "STM Studies of Thin Films, Clusters, and Other Nanostructures." (Division Sponsor: W.F. Egelhoff, Jr.)

**August 4, 1993**

Garnett Bryant, U.S. Army Research Laboratory, Adelphi, MD, "Electrons and Holes in Quantum Dots." (Division Sponsor: T. Jach)

**August 18, 1993**

Neal D. Shinn, Sandia National Laboratory, Albuquerque, NM, "Spectroscopy of Bi-Metallic Epitaxy and Interfaces." (Division Sponsor: C.J. Powell)

**September 14, 1993**

Victor Henrich, Yale University, New Haven, CT, "Transition Metal Surfaces: Single Crystal Studies of Electronic Structure, Chemisorption, and Metal/Oxide Interface Formation." (Division Sponsor: S. Robey)

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

**May 2-7, 1993**

Conference on Extreme Value Theory and its Applications, NIST, Gaithersburg, MD (Division Sponsor: L.A. Currie cooperated with the Statistical Engineering Division in organization and chair of Environment sessions)

**May 20-21, 1993**

Sixth East Coast Workshop on Secondary Ion Mass Spectrometry, IBM East Fishkill, Hopewell Junction, NY (J.G. Gillen)

**July 21, 1993**

Meeting of ISO/IUPAC representatives on Detection Limits in Metrology, FDS, Washington, DC (L.A. Currie assisted with organization)

**12. Other**

**a. Software Development**

Zeissler, C.J., Image Processing Command Enhancements to NIH Image for VRD Application (Second Version June 1993).

**b. Faculty Appointment**

**R.L. Kurtz**

Associate Professor of Physics and Astronomy, Louisiana State University, Baton Rouge, LA

**R.L. Stockbauer**

Professor of Physics and Astronomy, Louisiana State University, Baton Rouge, LA

## VII. Thermophysics Division (838)

Richard F. Kayser, Chief

### A. Division Overview

The Thermophysics Division conducts research in three major areas: the thermophysical properties of fluids and fluid mixtures; advanced separation processes; and pressure, vacuum, and leak-rate measurements and standards.

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 more recently, 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 membrane separations, supercritical fluid extraction, electrochemical 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 in monitoring and controlling processes and in assuring 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  $10^{-8}$  mol/s) and offers precision measurement workshops in these areas.

During FY93, approximately 40% of the Division's funds derived from other agencies and organizations, 5% from the NIST Standard Reference Data Program, and 5% from calibrations in the areas of pressure, vacuum, and leak rate. The Division provided technical services to the Department of Energy (several offices), the Department of Defense (all branches), the National Aeronautics and Space Administration, the Environmental Protection Agency, Sandia National Laboratory, and the Johns Hopkins Applied Physics Laboratory. In addition, the Division performed a substantial amount of work for industry through the Gas Research Institute, the Gas Processors Association, the Electric Power Research Institute, the Air Conditioning and Refrigeration Technology Institute, and individual firms.

During FY93, 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 most promising alternatives at present are incompletely fluorinated ethane-, methane-, and propane-based compounds and their mixtures. The objective of the Division's program is to acquire highly accurate thermophysical properties data for these fluids 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. Significant accomplishments during FY93 include the completion of comprehensive measurements and correlations of the properties of HFC-32 ( $\text{CH}_2\text{F}_2$ ), HCFC-123 ( $\text{CHCl}_2\text{CF}_3$ ), HCFC-124 ( $\text{CHFClCF}_3$ ), and HFC-125 ( $\text{CHF}_2\text{CF}_3$ ) for the air conditioning and refrigeration industry; completion of an extensive update of the tables and charts in the ASHRAE Handbook of Fundamentals -- a reference volume that is distributed to over 50,000 practicing engineers worldwide; and completion of a comprehensive analytical database and compendium of methods for analyzing alternative refrigerants and related compounds for publication by the CRC Press.

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 (12 new ones) and mixtures with as many as five components; calculations for mixtures are based on data for 62 mixtures (22 new ones). To date, the NIST Standard Reference Data Program (SRDP) has sold several hundred copies of REFPROP, which makes it one of the most popular databases that SRDP distributes. 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, which has extensive industrial and international participation.

Future efforts in the area of alternative refrigerants will concentrate more on the identification and characterization of alternatives for the HCFCs, especially HCFC-22 ( $\text{CHF}_2\text{Cl}$ ). The emphasis will be mostly on mixtures, since there are no obvious pure fluids that could serve as substitutes for the fluids currently in use. To help industry replace the HCFCs, it will be necessary to develop more accurate methods to calculate the properties of mixtures, especially mixtures that contain both polar and non-polar components.

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 yet generic thermophysical properties are essential to design and evaluate the performance of power plants and refrigeration systems and to optimize their economic performance. New programs in this area are focusing on mixtures of ammonia and water 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. With regard to mixtures of ammonia and water *vis-a-vis* water, recent developments indicate that such mixtures may offer 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. Accurate properties data for mixtures of ammonia and water are also important in the design and operation of absorption refrigeration systems.

The properties of natural gas mixtures and their 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 is supporting 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 and natural gas pipelines. A longer-term goal is to devise methods to separate the contaminants from natural gas distribution systems.

As another major activity, the Division maintains the Fluid Mixtures Data Center (located in Boulder, CO) and the Polar Fluids Data Project (located in Gaithersburg, MD) for the NIST Standard Reference Data Program (SRDP). The Fluid Mixtures Data Center compiles and evaluates data on the thermodynamic and transport properties of industrially important fluids and fluid mixtures and produces several well-known microcomputer databases for predicting

thermophysical properties, e.g., the NIST Thermophysical Properties of Hydrocarbons Database (SUPERTRAPP), which enables the user to calculate phase equilibria, single-phase properties, and transport properties for 116 pure fluids and fluid mixtures with as many as 20 components. These databases are all available through the SRDP. During FY93, the Data Center expanded considerably the capabilities of the NIST Mixture Properties Database (NIST14) and increased from 12 to 17 the number of fluids in the NIST Thermophysical Properties of Fluids Database (NIST12). The Data Center also contributed significantly to REFPROP, described above, and to the Division's work on water and aqueous systems -- the two areas in which the Polar Fluids Data Project has primary responsibility. In fact, the Polar Fluids Data Project, the Fluid Mixtures Data Center, and the Process Measurements Division are collaborating on a project aimed at using supercritical water to oxidize hazardous and toxic wastes. This technology exploits the fact that organic and certain inorganic materials can be hydrolyzed and oxidized to mostly innocuous products under the relatively mild conditions of water above its critical point. The Division's recent research on NaCl, CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> in water at high temperatures provides an excellent starting point for future efforts to develop more comprehensive models for multicomponent aqueous solutions containing salts, CO<sub>2</sub>, air, oxygen, and organic and inorganic compounds; the phase behavior of such solutions from room temperature to above the critical point is crucial for the design of supercritical water oxidation processes.

At the end of FY93, the Division transferred control of REFPROP from the Polar Fluids Data Project to the Fluid Mixtures Data Center and consolidated these two programs into a single data center in Boulder called the Fluid Properties Data Center. These changes are consistent with the overall directions of the programs on alternative refrigerants and aqueous systems and concentrate all of the Division's computerized databases in one place. Future efforts in the Fluid Properties Data Center will focus on consolidation of the databases and on structure-based modeling, which will involve the development of techniques for estimating chemical and physical properties from molecular information alone. This will include the development of accurate models for mixtures of chemically and/or physically dissimilar components, which is an important goal of the program on thermophysical properties.

The development of new thermophysical properties apparatus progressed well during the past year. The current program is the continuation of an intensive effort that was initiated in the early 1980s to improve the thermophysical property measurement capabilities of the U.S. The major objectives are to develop state-of-the-art experimental apparatus that can be used to measure the thermophysical properties of a wide range of fluids and fluid mixtures important to the chemical and energy-related industries. These new apparatus will make it possible to study a wide range of complex fluid systems under conditions which have been previously inaccessible. The specific measurement capabilities completed during the past three years (denoted by italics) or under development include new apparatus for transport properties (*tantalum-hot-wire thermal-conductivity apparatus*, vibrating-wire viscometer), thermodynamic properties (dual-sinker densimeter, *high-temperature vibrating-tube densimeter*, total-enthalpy flow calorimeter), phase equilibria properties (recirculating phase

equilibria apparatus, *low and high-pressure ebulliometers, re-entrant radio-frequency resonator*), and dielectric properties (*concentric-cylinder dielectric-constant apparatus*). The new high-temperature vibrating tube densimeter and the re-entrant radio-frequency resonator for detecting phase transitions non-visually both have commercial possibilities. They 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.

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 and modified carbon dioxide. Much of the Division's other research on process separations has an environmental focus, 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 the combustion products ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) from a fluidized-bed waste incinerator while retaining other species, and one aimed at separating  $\text{H}_2\text{S}$  from natural gas. Membrane technologies hold the promise of high separation factors in a simple one-stage process with associated low-energy requirements at moderate temperatures. The long-term goals are to understand the relationship between the membrane casting process and the microstructure of the membrane and between the microstructure of the membrane and its separation characteristics. Two other areas in which work has been initiated are electrochemical separations and adsorption. In the first case, the goal is to develop, refine, and scale-up the technologies required to separate both organic and inorganic pollutants from mixed environmental wastes and from aqueous industrial effluent streams; in the second case, the initial goal is to evaluate the state of the art of low-cost sorbents for separating a wide variety of metals from aqueous waste streams. Aqueous effluents account for 99 percent of the waste generated by the chemical process industry.

In the area of pressure measurements near and above atmospheric pressure, the Division has established excellent relations with the major U.S. manufacturers and users of pressure gages. Examples include a leadership role in the development of recommended practices for the calibration and use of piston gages, and participation in a CRADA (Cooperative Research and Development Agreement) with one of the manufacturers to characterize newly designed large-diameter (50 mm) piston gages made of an advanced material that can be machined to extremely close tolerances (500 nm). The first evaluations of the new gages have been very positive and indicate that the pistons are some of the roundest parts ever made. This project has the potential to lead to a new type of primary pressure standard in the important range near atmospheric pressure.

There have been several significant advances in the measurement of pressure near and below atmospheric pressure, i.e., in the vacuum area. These have ranged from the development of new standards and calibration services to research on new vacuum instrumentation. For example, recent improvements have lowered the uncertainty of the ultrasonic interferometer manometer, already NIST's most accurate pressure standard, and work on vacuum instrumentation has gone beyond efforts to characterize performance to the development of improved instruments. The successful development of an improved spinning rotor gage (SRG) controller will undoubtedly lead to commercial use in a variety of applications, and efforts to develop improved low-pressure transfer standards are well underway.

Many of the advances in the vacuum area address problems facing the semiconductor industry as it strives to increase product yield and quality. The first of these was the completion of a new orifice-flow primary pressure standard that fills a gap in NIST's primary pressure standards where many important industrial processes operate, including sputtering and plasma processing of semiconductors. The new system is ideal for studying flow phenomena in the transition range between molecular and viscous flow, and experimental and modeling work on the behavior of conductances in that range has established the basis for new types of vacuum calibration systems, including one that can be used for the *in situ* calibration of partial pressure analyzers in semiconductor processing systems. A second noteworthy accomplishment was the completion of a new water-flow standard that allows the generation of water vapor at pressures from below  $10^{-7}$  Pa to almost  $10^{-1}$  Pa. Water is a ubiquitous contaminant in vacuum systems, and quantitative measurements are crucial in the processing of semiconductor materials. These programs are part of a longer-term effort to develop multi-gas, *in situ* partial pressure measurement methods and standards for calibrating vacuum and semiconductor process instrumentation for use with other active gases, and ultimately, with process gases. A growing part of this research is the use of non-intrusive, species-specific optical techniques for performing quantitative measurements of low gas densities and compositions. During the past year, the Division completed the first quantitative resonance-enhanced multiphoton ionization (REMPI) measurements on carbon monoxide. The measurements extended over six decades of density, well into the ultra-high-vacuum (UHV) regime, both with and without overwhelming backgrounds of nitrogen. Future investigations will include both infrared absorption and laser-induced fluorescence measurements.

FY93 was an excellent year from the point of view of recognition. Dr. Michael R. Moldover received the honor of being elected a Fellow of the Acoustical Society of America for his pioneering research on spherical resonators for measuring the speed of sound in gases with unprecedented accuracy. Dr. J.M.H. (Anneke) Levelt Sengers received an award from the American Society of Mechanical Engineers for her vision and leadership in the field of utility and steam generation. Dr. Archie P. Müller received the Department of Commerce Bronze Medal for developing a unique high-speed laser interferometric technique for measuring the thermal expansion of solid materials at high temperatures. Dr. Charles R. Tilford received the NIST Edward Uhler Condon Award for distinguished achievement in



written exposition for his lucid review article entitled "Pressure and Vacuum Measurements", which appeared in *Physical Methods in Chemistry, Second Edition, Volume Six: Determination of Thermodynamic Properties*. Dr. Daniel G. Friend received a NIST Measurement Service Award for his outstanding contributions to the NIST Standard Reference Data Program, and in particular, for his outstanding leadership of the Fluid Mixtures Data Center.

There were two significant organizational changes during FY93: the creation of the Process Separations Group and the abolishment of the Subsecond Thermophysics Group. As a result of these changes, the Division now consists of five groups: Properties of Fluids (Boulder, CO), Fluid Science, Process Separations (Boulder, CO), Pressure, and Vacuum. The following Technical Reports describe the activities and major accomplishments of these groups in more detail.

**B. Selected Technical Reports  
(Thermophysics Division)**

**1. Supercritical Fluid Extraction of Pharmaceutical Natural Products**

**T.J. Bruno, B.N. Hansen, and A.F. Lagalante (University of Colorado)**

During the past five years, there has been renewed interest in the use of supercritical extraction for industrial separations. It is clear, however, that candidate systems must be chosen carefully. The best candidate solutes are high-cost, low-volume commodities that require a nontoxic solvent for processing. This includes such products as pharmaceuticals, food flavorings, and essential oils. The Division's past research in this area produced an economical design for the extraction of natural  $\beta$ -carotene from an aqueous broth, and a novel continuous separator for the process. Currently, the products of interest include taxol (an anti cancer drug), capsaicin (a drug used for the treatment of shingles, a common complication of AIDS), vitamins A and E, and surfactants such as lauric acid and phospholipids (used in the treatment of infant respiratory distress syndrome).

Although carbon dioxide is the classical supercritical fluid solvent, the program has focused instead on the use of several very promising alternative refrigerants. These fluids offer a polar, yet pure alternative to carbon dioxide and modified carbon dioxide. During the past year, major outputs have included supercritical solubility studies of several pharmaceuticals in alternative refrigerants such as R32, R22, R124, R125, R116, and R134a. For this work, several novel instruments were developed and described in publications.

In addition to this experimental research program, a more accurate method for calculating the solubility parameter of supercritical fluid solvents has been developed. This is important because the shift away from carbon dioxide as the exclusive solvent will require thorough consideration of the cohesion parameters of not just the solute, but of the new solvents as well.

**2. Numerical Modeling of Electrochemical Separation Processes**

**A.P. Peskin, G.R. Hardin, B. Louie, and T.J. Bruno**

Dilute mixed-waste streams are an environmental challenge in need of cost-effective solutions. Electrochemical cells offer a potentially efficient means of separating dilute pollutants from large volumes of process effluents. Previous attempts to apply this technology have been promising, but this work typically produced cells with short lifetimes and low efficiencies. A fundamental understanding of electrode performance is badly needed to devise efficient designs.

The Division is focusing on moving-bed electrode systems, with the initial emphasis on numerical modeling. This work is an outgrowth of previous research on cathodic oxidation reactions for the destruction of organic pollutants and on the modeling of electrodeposition and corrosion. The present capability of modeling complex physicochemical fluid dynamics is the result of an intensive two-year effort to develop and apply the necessary computational tools. The current software makes it possible to model momentum, heat, and mass transfer with homogeneous and heterogeneous chemical reactions. It also enables the user to model moving boundaries such as those encountered in surface growth with shape change and in moving free surfaces.

During the past year, the numerical modeling team analyzed electrodeposition into a small cavity with electrolyte flowing across the top. The model includes fully-coupled flow and mass-transport that dynamically tracks the spatially-nonuniform growth of the deposited layer. The model predicts shape changes of the cathode as cations are deposited under a variety of flow regimes. The distribution of current, and thus the local rate of deposition, depends upon the resultant shape of the deposited surface.

The aim of another modeling effort is to describe the concentration boundary layers of electrolytic species at a titanium anode during the separation of pollutants from waste streams. The chemical species of interest at the interface are protons, hydroxide ions, and polluting components such as benzene and  $\text{CHCl}_3$ . In the future, experimental studies of the components adsorbed onto the titanium anode will be compared with neutron scattering studies of the anodic surface. Additional simulations with applied voltage will describe the efficiency of these systems in electrochemical cleanup over specified periods of time.

### **3. Separation of Trace Contaminants from Natural Gas**

**T.J. Bruno and J.E. Mayrath**

Natural gas is a complex, often two-phase mixture of organic and inorganic constituents, most of which are naturally occurring but some of which are introduced intentionally during processing. The gas phase consists of approximately 40 major constituents, while the liquid phase can contain between 350 and 450 compounds. Some of the constituents in both the gas and liquid phases are a source of concern, and the Division has been involved with the gas industry in devising effective separation strategies.

A major focus of the work during the past year continued to be the separation of trace levels of heavy halogenated organics such as polychlorinated biphenyls (PCBs). The solid- and liquid- phase vapor pressures of six pure PCB congeners were measured with three separate gas- saturation instruments that were designed and constructed specifically for these types of materials. This work is significant in that it allows modeling of the transport of PCBs in natural gas systems and provides insight into the relative contribution of the gas and liquid

media to the total transport overhead. To support the vapor-pressure measurements, differential scanning calorimetry was performed on each congener to determine possible phase changes. In addition, measurements were completed of the enthalpy of adsorption of PCB congeners on steels and polymers to assist in the design of effective pipeline cleanup strategies. Also completed was a study of the gas-to-liquid solubility characteristics of individual congeners in typical natural-gas condensates. All of this work is necessary for the rational design and implementation of separation systems for natural-gas distribution lines.

#### 4. Chemically-Specific Gas, Vapor, and Liquid Membrane Separation Systems

J.J. Pellegrino, M.K. Ko, L.A. Watts, M.R. Yetzbacher, C. Baca (University of Colorado), D. Wang (University of Colorado), Y.S. Kang (Korean Institute of Science and Technology, Korea), B. Logsdon (EG&G), D. Stull (EG&G), B.R. Mattes (Los Alamos National Laboratory), R. Knecht (Colorado School of Mines), J.P. Agarwala (University of Colorado), P. Todd (University of Colorado), and E. Tracey (University of Colorado)

Membrane separations use a selective molecular barrier between two process phases. Simplicity of equipment, more efficient use of materials and space, and energy savings are the main incentives for this technology's advancement into the industrial sector. Processing equipment based on membranes is now being applied to increase the efficiency of many manufacturing processes and to help meet environmental quality goals in waste reduction and remediation and domestic water supplies. Barriers to greater usage of membrane processes include adsorption of foulants, the lack of *a priori* predictive capabilities for transport properties of mixtures in a particular membrane, lack of simple ways of designing optimum process configurations, lack of data and experience on complex process streams, and the high cost of equipment. Our projects address many of these barriers.

Improved data and 3-phase models have been developed for studying the microstructure of phase-separated polymers (e.g., ion-exchange polymer polyperfluorosulfonic acid) useful in fuel gas separations ( $H_2S$ ,  $CO_2$ ,  $CO$ ,  $H_2$ ,  $CH_4$ ,  $O_2$ ), refinery operations (olefin production), and fuel cells. Measurements on composite films of this polymer and a redox catalyst to purify  $H_2S$ -contaminated natural gas at room temperature in a single step have begun and are yielding promising results. This technology may be significant for utilizing much of the dispersed, high-sulfur natural gas reserves in the U.S. Critically evaluated experimental data have been obtained on commercial gas separation membranes as possible molecular filters for the stack gases from hazardous waste incinerators. Measurements of  $O_2$  and  $N_2$  solubility in conducting polymers have been conducted. These polymers may provide a means to produce low-cost pure oxygen for reducing pollution from combustion sources. Spreadsheet-based models have been developed for defining economically optimum process designs involving membranes and absorption-stripping hybrid processes for natural gas purification. The selective transport of lead in aqueous electrolyte streams has been demonstrated with a new

immobilized liquid membrane concept for highly specific electro dialysis processes. The objective of this work is to use electrical energy to remove just the trace levels of toxic metals from water supplies, without expending energy on common ions like Na, K, and Ca. Further results have been obtained on a NIST-developed technique for determining total protein adsorption on membranes used in biotechnology and water purification. This work addresses the fouling of membranes used in aqueous separation processes.

## 5. Chemical Analysis Procedures for Alternative Refrigerants

T.J. Bruno, P.D.N Svoronos (City University of New York), and M. Caciari (Lupton High School, Fort Lupton, CO)

The calculation of reliable and accurate thermophysical properties for alternative refrigerant fluids depends upon measurements performed on well-characterized fluid samples. A major focus of the Thermophysics Division's research program on alternative refrigerants has therefore been the development of the needed chemical analysis technology to thoroughly characterize the 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, including chromatographic, spectroscopic, and physical properties data.

In terms of new instrumentation and approaches, a new device and technique for chromatographic cryofocusing/cryotrapping have been developed and published. A novel low-temperature cell for infrared spectrophotometry was designed, constructed, and patented, and a new approach to high-pressure ultraviolet spectrometry has been published. A new sample pre-concentration device has also been developed and patented.

The most significant output of this effort has been the completion of a comprehensive analytical database on alternative refrigerants and related materials, which will be published as a two-part handbook by CRC Press. The first part will be a compendium of methods that have been used in the analysis of alternative refrigerant fluids. It will include detailed descriptions of the devices, instrumentation, and analytical protocols developed within the Division. The second part will be a collection of analytical data on each fluid. This will include mass, infrared, ultraviolet-visible and nuclear magnetic resonance spectra ( $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$ ); chromatographic retention parameters; and physical property data useful for identification. This information will provide the basis for rational impurity identification and sound strategies for quantitative analysis.

## 6. Release of New Version of REFPROP

M.L. Huber, J.S. Gallagher, M.O. McLinden, M.R. Moldover, and G. Morrison

REFPROP is a user-friendly PC program incorporating a database developed by the Thermophysics Division. The package is used to screen a wide range of environmentally-acceptable refrigerants as possible replacements to currently-used refrigerants. REFPROP generates tables of thermophysical properties that are used by engineers to predict the efficiency and capacity of machinery that will employ alternative refrigerants. In contrast with most other software packages, the FORTRAN source code for REFPROP is included in the package. Many customers have incorporated this NIST-produced code into their own proprietary models for specific applications.

During FY93, REFPROP 4.0 was completed. REFPROP 4.0 provides data for 38 refrigerants (12 new ones) and their mixtures (of up to 5 components). For these fluids, the package estimates the thermodynamic properties (including phase equilibria), transport properties, and other properties such as interfacial tension, dipole moment, and polarizability.

REFPROP 4.0 contains highly accurate modified Benedict-Webb-Rubin (MBWR) equations of state for 11 fluids. The MBWR equation of state for R134a correlates the most recent accurate thermodynamic information for this important replacement refrigerant and it also serves as the reference function for an extended corresponding states (ECS) model for the thermodynamic properties of the other pure fluids on the REFPROP menu (except ammonia). The ECS model is used to estimate the transport properties of these fluids and their mixtures. For ammonia, the highly accurate Haar-Gallagher equation of state is used.

The Carnahan-Starling-DeSantis model is available for all the fluids in REFPROP (except ammonia) and it is used for all calculations of the thermodynamic properties of mixtures. Mixing parameters derived from experimental data are available for 65 binary pairs (22 new ones); for other pairs, a rule is provided for predicting mixing parameters from dipole moments.

Over 200 copies of REFPROP have been sold by the Standard Reference Data Program. REFPROP has been adopted as a standard by the Air Conditioning and Refrigeration Institute; it is also distributed by the American Society of Heating, Refrigerating, and Air Conditioning Engineers (ASHRAE).

The development of REFPROP is continuing. Ultimately, it is expected that REFPROP will include all stable, small molecules and their mixtures that could plausibly be used as working fluids in thermal machinery. For these fluids, REFPROP will deliver the most accurate data available in the form that is most useful to the engineering community.

## 7. Thermodynamic Properties of Alternative Refrigerants

J.W. Magee, M.O. McLinden, G. Morrison, L.A. Weber, D.R. Defibaugh, C.D. Holcomb, J.B. Howley, M.L. Huber, S.L. Outcalt, K.A. Gillis, A.R.H. Goodwin, M.R. Moldover, and W.M. Haynes

The Thermophysics Division has been involved with refrigerants for over ten years. The early work was in conjunction with studies of refrigerant mixtures in heat pumps by the NIST Building Environment Division. With the increasing concern in the mid-1980's about ozone depletion caused by chlorofluorocarbons (CFCs), the Division's work rapidly evolved into a comprehensive program to study and characterize a wide variety of alternatives to the CFCs and HCFCs (hydrochlorofluorocarbons). The Division's activities consist of experimental measurements, compilation of literature data, correlation of data, and theoretical modeling. Accurate values of the thermodynamic properties are vital to evaluate the performance (energy efficiency, capacity, etc.) of new fluids in refrigeration applications and to design refrigeration equipment using the alternative refrigerants.

In FY93, the Division completed comprehensive measurements of the thermodynamic properties of refrigerants R32 and R125; these two fluids are leading candidates to replace HCFC-22, either as pure components or as constituents of mixtures. The measurements include vapor pressure, pressure-volume-temperature (PVT) behavior, isochoric heat capacity, speed of sound, dielectric constant, surface tension, and the triple-point and critical-point parameters; the measurements cover very wide ranges of temperature and pressure in the liquid, vapor, and supercritical states and are of state-of-the-art quality. Similar measurements are in progress for R152a and R143a.

Not all potential refrigerants warrant comprehensive measurements. Limited data were obtained for R143, R236ea, R227ea, R245ea, and R142b; these data consist of vapor pressure and liquid density measurements over a temperature range of roughly 0 to 100°C along with a critical point determination. These data allow a preliminary assessment of a potential refrigerant.

A comprehensive survey and compilation of literature data for the HFC (hydrofluorocarbon) and HCFC refrigerants were carried out in FY93. This work was in support of our modeling and correlation efforts and of the activities of International Energy Agency Annex 18 (see report #9).

The new wide-ranging measurements for R32 and R125, together with literature data, were used to fit high-accuracy, standard-reference-quality modified Benedict-Webb-Rubin (MBWR) equations of state. These equations were developed using a multivariable fitting technique that allows a simultaneous fit of all of the experimental data, including "higher order" data such as heat capacity and speed of sound; they are valid from near the triple point to above 400 K. These equations, together with MBWR equations developed

previously for R134a, R123, and R124, have been incorporated into Version 4.0 of the REFPROP computer package, which is available from the NIST Standard Reference Data Program (see report #6).

Refrigerant mixtures are becoming increasingly important as alternative refrigerants, particularly as replacements for HCFC-22. Mixture data are required to determine the "mixing parameter" in our mixture models. Selected vapor-liquid equilibria (VLE) measurements were completed on eleven mixtures in FY93: R125/R115, R125/R134a, R125/R143a, R134a/R152a, R134a/RC270, R134a/R290, R134a/R600, R152a/RC270, R152a/R290, R152a/R600, and R152a/R600a. Moreover, vapor-phase PVT measurements were completed on 5 mixtures: R32/R125, R32/R134a, R125/R134a, R125/R143a, and R134a/R152a; these measurements yielded cross second virial coefficients in addition to mixing parameters. The data on these mixtures bring to 65 the number of binary pairs for which experimentally-based mixing parameters are included in REFPROP.

## 8. Transport Properties of Alternative Refrigerants

R.A. Perkins, A. Laesecke, D.G. Friend, M.L. Huber, D.C. Ripple, D.E. Diller, H.M. Roder, V. Lindqvist (University of Colorado), C.A. Nieto de Castro (University of Lisbon, Portugal), and O. Matar (Imperial College, London)

The measurement and correlation of transport properties for alternative refrigerants are complementary to the study of their equilibrium 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 insulations manufactured using alternative refrigerants. Pure fluids were the primary focus of our efforts during FY93, but two mixtures containing R32 and R125 also were studied.

The Thermophysics Division has the capabilities to study the thermal conductivity and viscosity of these new alternative refrigerants over an extremely wide range of temperature and pressure using a variety of measurement techniques. Transient hot-wire thermal conductivity instruments are available which cover the temperature range from 60 to 750 K at pressures to 70 MPa. For measurements of polar refrigerants, these instruments can operate either with bare platinum hot wires using a polarization technique or with an electrically-insulated tantalum hot-wire cell. These transient hot-wire instruments can also be operated in a steady-state mode for dilute gas thermal conductivity measurements ( $< 0.1$  MPa). Two torsionally-oscillating quartz-crystal viscometers are available which cover the temperature range from 60 to 600 K at pressures to 70 MPa. A capillary viscometer is available which covers the temperature range from 250 to 330 K at pressures to 1 MPa.



The Thermophysics Division is participating in a round-robin series of transport property measurements on R134a sponsored by the IUPAC (International Union of Pure and Applied Chemistry) Transport Properties Subcommittee. This round-robin test will assess the accuracy of transport property data obtained on a well characterized sample using independent techniques at NIST (U.S.), Imperial College (U.K.), Sheffield University (U.K.), University of Lisbon (Portugal), Aristotle University (Greece), Keio University (Japan), Technical University of Munich (Germany), and University of Rostock (Germany).

The correlation and prediction of the transport properties of alternative refrigerants is the final product. Based on data measured in the Thermophysics Division and obtained from the literature, correlations have been developed for specific fluids, 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.

Comprehensive measurements of the thermal conductivity and viscosity of R134a, R32, R123, R124, R125, and E134 have been completed in the liquid, vapor, and supercritical gas phases. Thermal conductivity measurements have been completed for the R32/R125 azeotropic mixture and the R32/R125 equimolar mixture in the liquid, vapor, and supercritical gas phases. Vapor-phase thermal conductivity measurements have been completed from 280 to 330 K on E245, E263, R143, R227ea, R236ea, and R245ca. Saturated-liquid viscosity measurements have been made from 250 to 310 K on R134a, E134, E245, R32, R124, R125, and the equimolar mixtures of R125/R134a, R32/R134a, and R32/R124. The Division received support for this work from the air conditioning and refrigeration industry, the Department of Energy, and the Environmental Protection Agency.

## **9. International Activities on CFC Alternatives**

**M.O. McLinden, R.A. Perkins, and W.M. Haynes**

The Thermophysics Division initiated and serves 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, 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 a comprehensive, internationally-accepted properties bulletin. 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 Cornell University.

The focus of Annex efforts in FY93 was the completion of an evaluation of experimental data and equations of state for refrigerants R123 and R134a. This is the crucial step for the Annex to select the best equation of state for the properties of these two leading alternatives to the fully halogenated CFC refrigerants. The University of Idaho and Imperial College, London completed their comparisons of the available data to three equations of state for R123 and four equations for R134a. They were assisted by NIST and Keio University, Japan in this task. Based on these comparisons, the equation of state developed at NIST (see report #7) was selected by the Annex to become the de facto international standard for R123; an equation from the University of Hannover in Germany was selected for R134a. These equations will form the basis for an international properties bulletin. Work also continued on the compilation of thermophysical property data for more than a dozen alternative refrigerants. The very successful survey of world-wide research on the measurement and modeling of refrigerant thermophysical properties is being updated. As with the first survey (published in 1991 as NIST Internal Report 3639), NIST coordinated the survey and was assisted by Keio University, Japan and the National Engineering Laboratory, United Kingdom; Texas A&M University has compiled the survey responses and is preparing the final report. The original three-year term of the Annex has been renewed. The focus of future work will shift to replacements for R22 and other HCFC refrigerants.

The Division also is participating in IUPAC activities on the transport properties of the alternative refrigerants. The highly polar HFC and HCFC refrigerants present special difficulties for some of the standard techniques for measuring thermal conductivity and viscosity. An international round-robin test series is underway on a "standard" refrigerant (R134a) for quality control of thermal conductivity and viscosity measurements; see report #8.

The Division is participating in the third technical reassessment associated with the Montreal Protocol on Substances that Deplete the Ozone Layer, the international treaty that regulates the production of CFCs. This review is coordinated by the United Nations Environment Programme. M.O. McLinden serves on the panel responsible for the "Technical Options Report" on refrigeration and air-conditioning uses of CFCs and is acting as lead author for the "Refrigerant Data" section in this report. This process was initiated in 1993 and will serve as input for the renegotiation of the phase-out timetable and other provisions of the Protocol to take place in 1995.

The Division has worked very actively with the American Society of Heating, Refrigerating and Air Conditioning Engineers (ASHRAE). (Although based in the U.S., ASHRAE is an international organization that "leads the way" for the entire refrigeration industry.) M.O. McLinden coordinated the update of the tables and charts of refrigerant properties in the 1993 ASHRAE Handbook of Fundamentals—a reference volume that is distributed to over

50,000 practicing engineers worldwide; this update included the addition of six new alternative refrigerants. Dr. McLinden also served on the ASHRAE committee responsible for classifying the alternative refrigerants; classification is required by many building codes before a new refrigerant can be used in commercial and residential systems.

## 10. Advances in the Theory and Modeling of Thermophysical Properties

**D.G. Friend, M.L. Huber, J.C. Rainwater, H.J.M. Hanley, J.M.H. Levelt Sengers, J.S. Gallagher, D.P. Fernandez (Argentine National Atomic Energy Commission, Argentina), L.J. Van Poolen (Calvin College), and J.A. Given**

The theoretical and modeling activities within the Division complement the experimental activities and have the goal of providing accurate calculational algorithms and predictive capabilities to represent property surfaces of a wide variety of pure fluids and mixtures. The modeling efforts encompass a very broad range of state variables and, where possible, are based on theoretically-based validated formulations. The Division currently supports five computerized databases which are being distributed through the Standard Reference Data Program of NIST. New releases of the NIST Mixture Property Database (NIST14, Version 9.08) and the NIST Thermophysical Properties of Pure Fluids Database (NIST12, Version 3.1) were completed during FY93; see report #6 for a discussion of a major update of the NIST Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Database (REFPROP).

The increasing importance of supercritical aqueous oxidizing reactions and the identification of the binary ammonia-water system as an important working fluid in power generation cycles have led to several projects related to aqueous mixtures. The development of standard reference thermodynamic surfaces for the water/carbon dioxide and water/nitrogen binaries based on a one-fluid corresponding states principle has been completed. A preliminary study of the ammonia/water system based on two-fluid extended corresponding states (ECS) using correlated shape factors has been concluded, and there is a current effort to implement a more accurate ECS model for these systems. For this promising model, exploration of the critical loci and phase boundaries of aqueous systems is underway. A formulation for the limit of homogeneous nucleation in pure steam, as well as for the boundaries between metastable and stable thermodynamic states, have been compared to available data. A database on the dielectric constant of water and steam has been completed, and a new formulation based on the ITS-90 temperature scale is being finalized.

A review article on the calculation and prediction of transport properties from the ECS model has been completed. The newest version of the refrigerants calculational database includes an option to determine the enhancement of the pure-fluid thermal conductivity associated with critical region fluctuations based on mode-coupling theory combined with the ECS model.

To describe the phase diagrams of mixtures at high pressures, modifications to the nonclassical Leung-Griffiths model have been developed. Examination of a model that includes both vapor-liquid and liquid-liquid equilibria (VLE and LLE) is in progress, and the perturbative effect of LLE on the VLE surface for Type 2 mixtures is being studied. For Type 1 mixtures, with a single critical line which is monotonic in temperature, the basis for the conclusion that the "hidden" field variable, which cannot be calculated solely from PVTx data, can be made to coincide with the composition variable along the critical line has been strengthened. Also, a method to extract the critical exponent  $\beta$  from isothermal VLE data of certain dilute mixtures has been developed, and an examination of both classical and nonclassical models, as well as experimental data, is in progress in a study to determine the extent of the applicability of the standard nonclassical value.

The development of highly accurate correlations for the thermophysical properties of pure fluids has continued. In addition to the standard-reference-quality surfaces on refrigerants, discussed in report #7, new reference thermodynamic surfaces for heptane and isohexane are nearly complete. The simulated annealing approach to the structural optimization of correlating surfaces has been extended to multiproperty fits of the full thermodynamic surface. This approach is being tested on data for alternative refrigerants for equations with 8 to 12 terms chosen from a large bank of terms.

## 11. Studies of the Properties of Natural-Gas Mixtures

J.W. Magee, C.D. Holcomb, W.M. Haynes, J.B. Howley, and J.F. Ely (Colorado School of Mines)

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. This work has been supported primarily by the Gas Research Institute (GRI).

NIST has been a major participant in an international round-robin series of PVT measurements aimed at providing the natural-gas industry with PVT standard reference data (uncertainty of  $\pm 0.05\%$ ) for use in custody-transfer transactions. This project, which has been sponsored and managed by GRI, is a cooperative effort between U.S. and European interests in the natural-gas industry. Other participants in the project include Texas A&M University in the U.S. and Ruhrgas, van der Waals Laboratory, Gasunie, and Gaz de France in Europe. The five representative natural-gas mixtures used in the round robin were prepared at NIST; PVT measurements were performed at NIST, Ruhrgas, van der Waals Laboratory, and Texas A&M University; and the data evaluation was carried out at the van der Waals Laboratory. The major objectives of this study have been satisfied, and in some cases, exceeded. The agreement between these experimental values of the compressibility

factor and those calculated from American and European custody-transfer equations of state is approximately 0.03% in the major region of custody transfer. The results of this project will be published during FY94 as a NIST Monograph with joint authorship among the project participants.

In a related project sponsored by the Gas Processors Association (GPA), density measurements are being carried out on natural-gas-liquid components and mixtures. The purpose of this work is to improve the accuracy of ASTM (American Society for Testing and Materials) and API (American Petroleum Institute) standards for volume correction factors involved in custody-transfer calculations for natural-gas liquids. The experimental work is being performed at NIST, while the modeling is being done at the Colorado School of Mines. Saturated liquid density measurements have been carried out on propane, normal butane, normal pentane, isopentane, and isohexane at temperatures from 240 to 420 K; vapor densities have been obtained from about room temperature to 420 K. Measurements on binary mixtures of ethane and propane with ethane mole fractions of 0.35 and 0.65 are in progress on an isochoric PVT apparatus at temperatures from 200 to 400 K with pressures to 35 MPa. With the vapor-liquid equilibrium (VLE) apparatus, coexisting density and VLE 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.

During the past year, ASTM has adopted standards for the properties of the major components of natural gas (methane, ethane, propane, isobutane, normal butane) based on NIST Standard Reference Databases. Also adopted was a revised version of a standard for liquefied-natural-gas densities based on measurements and models developed at NIST.

## **12. Extension of Vibrating-Tube Densimetry to High Temperatures**

**R.F. Chang and M.R. Moldover**

The objective of this project is to develop a precise, easy-to-use densimeter that works at temperatures up to 400 °C. Half a dozen prototype vibrating-tube densimeters have been constructed and tested at temperatures up to 450 °C. Many additional tests were made using mock-up densimeters with vibrating wires made from a wide variety of alloys. Several mechanical problems were identified and solved. However, all of the instruments tested showed some aging above 300 °C.

One prototype was calibrated with water in the temperature range 25-300 °C and the pressure range 0-14 MPa. The calibration was tested the following day by measuring the density of toluene in the temperature range 25-300 °C at a pressure of 14 MPa. The toluene data had a root-mean-square deviation from published data of 0.44 kg/m<sup>3</sup>, corresponding to 0.06% of the measured densities. Thus, a very useful instrument has been developed for

measurements under these conditions. Several novel design features have been included in a patent application. NIST's Office of Technology Commercialization is negotiating a license to this technology with the manufacturers of commercial vibrating-tube densimeters.

Above 300 °C, the resonance frequency of every densimeter made thus far increases slowly, even under vacuum. This phenomenon is not understood and is being studied further. Absent new results, the aging shall be circumvented by automating the measurement system so that only a few minutes will elapse between calibration of the densimeter and its use with a test fluid. This tactic will permit accurate laboratory measurements under a wide range of conditions; however, it is not suitable for field measurements.

### **13. Development of a Novel Reentrant Resonator for Dielectric Measurements**

**A.R.H. Goodwin and M.R. Moldover**

The objective is to develop a versatile, reliable, automated method of detecting the density changes associated with the onset of phase transitions in fluids, especially fluid mixtures. Such a method would be an economical alternative to those tedious conventional investigations of dew and bubble curves that rely on visual observation of the onset of liquid or vapor formation.

For this application, reentrant radio-frequency (rf) cavities that are resonant near 400 MHz were tested. As expected, upon phase separation of the sample, the resonance frequency changed because the dielectric constant of the sample within the annular "capacitance" portion of the cavity changed. The rf resonator is a much lower impedance device than conventional capacitors used at audio frequencies. Thus, these rf resonators can be used even when the test fluid is somewhat conducting. Furthermore, these rf resonators were designed such that they have no metal-insulator joints in critical locations. This design should be useful given that such joints are prone to failure when subjected to stress from thermal expansion and/or applied pressure.

The versatility of one prototype was demonstrated by using it for three tasks: (1) to measure the polarizability of argon to state-of-the-art accuracy, (2) to measure the dipole moment of 1,1,1,2,3,3-hexafluoropropane (designated R236ea by the refrigeration industry), and (3) to measure the dew-bubble curves of three mixtures of carbon dioxide + ethane under computer control.

An rf resonator for detecting phase transitions is being built to operate at temperatures up to 400 °C and pressures up to 20 MPa.

#### **14. Measurement of Critical Point Viscosity**

**R.F. Berg and M.R. Moldover**

The objective of this NASA-sponsored project is to test the theory of transport properties of fluids very near the liquid-vapor critical point. To date, a definitive test of the theory has not been possible on earth because of the very weak divergence of the viscosity as the critical point is approached and because the approach to the critical point is limited by the earth's gravity. Fluids within 4% of the critical density and 0.01% of the critical temperature are so compressible that the density near the bottom of a 1 mm-high sample exceeds the density near the top of the sample by 8% or more.

In recent years, experimental progress in this field has been led by the Thermophysics Division. A series of viscometers has been developed that achieves the necessary combination of low frequency (1 to 5 Hz), low shear rate (0.1 to 1 s<sup>-1</sup>), precise temperature control (0.1 mK), and high viscosity resolution (0.1%). Measurements have been completed near the critical points of xenon, carbon dioxide, four binary liquid mixtures of small molecules, polymer solutions, and microemulsions. The NIST results have stimulated theoretical work to re-calculate the exponent characterizing the divergence of the viscosity.

During FY93, the Division continued to develop a new viscometer of a novel design that will meet the criteria mentioned above but will add the capability of operating in the vibrationally noisy environment of the orbiting Space Shuttle. On the Shuttle, the gravity-induced density stratification is negligible and meaningful measurements will be made to within 0.6 millikelvin of the critical temperature of xenon. Remarkably, this new viscometer will survive the rigors of a Shuttle launch, and it will measure the viscosity of a near-critical xenon sample while dissipating only 1 picowatt of power within the sample.

#### **15. Neutron Scattering Studies of the Structure of Fluids**

**H.J.M. Hanley, G.C. Straty, C. Zukoski (University of Illinois), D. Peiffer (Exxon), S.K. Sinha (Exxon), F. Tsvetkov (Weissmann Institute, Israel), and R.H. Ottewill (University of Bristol)**

This program is concerned with 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. Particularly interesting are the behavior and properties of fluids under unusual experimental conditions, for example, near a phase transition, under shear, or in a gelation environment.

The studies described here involve measuring the structure factor by neutron scattering. Neutrons have several advantages as radiation probes, principally because the scattering is at

the level of the nucleus. Scattering from the nucleus means that isotopic substitution is a tool: selective substitution of D for H in a molecule, for example, is an effective trick to monitor only those parts of a molecule that one wants to see. Scattering from the nucleus also permits the technique of contrast matching, i.e., elements of a fluid (a given species in a mixture, or parts of a given molecule) can be made invisible to neutrons so that the scattering pattern results only from the portion that one wishes to observe. Matching is achieved by changing the background scattering length density (the neutron equivalent to the refractive index) to be equivalent to that of the element, rendering the element invisible.

The technique of contrast matching was used in two experiments performed at the NIST Cold Neutron Research Facility. In both cases, aqueous suspensions of hydrogenated polystyrene and deuterated polystyrene were used to mimic an atomic fluid mixture. The components were contrasted by altering the composition of the D<sub>2</sub>O/H<sub>2</sub>O solvent. The first set of experiments was conducted with experimentalists from the University of Bristol on dilute mixtures in equilibrium and under shear, using the shearing cell constructed for the neutron facility in 1991. Mixture structure factors were compared with statistical mechanical theory. The second set of experiments was carried out with staff from the University of Illinois on dense suspensions to test the density functional theory of freezing. The data were not always consistent with the theory, which implies that a reassessment of the theory is needed.

A program was continued with Exxon to investigate the structure of a 'living' polymer under a shear field. 'Living' polymers arise when small spherical micelles grow to form worm-like macromolecules. These macromolecules can themselves grow, can be broken by an external force, but can reform when the force is removed. Measurements of their growth rate and orientation under shear represent the current objectives of this segment of the program. A new facet was introduced by considering the micelle as part of a system with a clay mineral. Studies of how the organic micellar material adsorbs on bulk clay and on clay in the form of platelets have been initiated. Plans are underway to expand this segment of the program, since the results are most promising and could well impact the field of nanometer composite materials. This study also has strong environmental implications if the organic compounds and clay are chosen to represent pollutants and soil constituents.

This year a study of gelation has been initiated. Silica 'Ludox' has been gelled at equilibrium and under shear, and its structure has been examined. The neutron intensity patterns show that the final gel state is affected strongly by the shear at high volume fractions. This study is of considerable promise and will impact the industrially important areas of nanomaterials and sol-gel fabrication.



16. Measurement Services Provided by the Thermophysics Division in the Areas of Pressure, Vacuum, and Leak Rate

P.J. Abbott, S.W. Doty, R.G. Driver, C.D. Ehrlich, A.R. Filippelli, R.W. Hyland, J.P. Looney, W. Markus, C.R. Tilford, S.A. Tison, D.B. Ward, and B.E. Welch

The Pressure and Vacuum Groups of the NIST Thermophysics Division provide calibration and test services to both the domestic and international communities in the areas of pressure, vacuum, and leak rate. Vacuum and pressure calibrations span sixteen orders of magnitude, from  $10^{-7}$  Pascal (Pa) to almost  $10^9$  Pa, and leak rate calibrations now cover  $10^{-14}$  moles/second (mol/s) to  $10^{-6}$  mol/s. The two groups develop and maintain a wide variety of primary and secondary standards in support of these services.

Calibration income to the Division from the two groups totalled \$277K in FY93, 44% from the Pressure Group and 56% from the Vacuum Group. This was derived from calibration of 56 piston gages, 24 low pressure gages, 13 ionization gages, 19 spinning rotor gages, and 12 leaks. This level of work has remained fairly constant ( $\pm 10\%$ ) over the last five years for both groups. The volume of vacuum calibrations is down slightly in some areas, but the income is down even more (by 15%). The reduced income is due to fee reductions that reflect improved efficiency in some of the services. Vacuum and low-pressure gage calibration customers are still predominantly from the aerospace, defense, utility, and process (semiconductor, pharmaceutical) industries. The piston-gage calibration customers are distributed among the military, other foreign and domestic government laboratories, utility companies, the Department of Energy, manufacturers, and private industry.

A detailed analysis this year of a nominal 4 MPa gas-operated piston-gage transfer standard allowed the Pressure Group to offer a Special Test Service based on this gage with reduced uncertainties at the three-sigma level in the 35 to 50 parts-per-million range. A review of the uncertainties of all of the vacuum standards is underway. This review is prompted by technical improvements in several of the standards, accumulated experience, and the need to conform to the new NIST policy on reporting uncertainties. The work to date indicates that there will be real improvements in the accuracies of some of the calibration services, in some cases by as much as a factor of two or three.

17. Improved Ultrasonic Manometry

R.W. Hyland, P. Farar, J.P. Looney, A.P. Müller, and C.R. Tilford

NIST has taken a unique approach in the design of high-resolution mercury manometers: the lengths of the mercury columns are determined from the change in phase of an ultrasonic signal transmitted through the mercury. This technique is automated, does not perturb the

temperature of the manometer, and achieves an unmatched imprecision of 0.01 micrometers in the column length measurement. Originally developed as a high-resolution, low-range (10 kPa) pressure standard, the Ultrasonic Interferometer Manometers (UIMs) have been progressively developed to cover the range up to 350 kPa. They are used to calibrate instruments which are commonly used as transfer standards in a number of industries and to establish the basis for other NIST pressure and vacuum standards.

Over the past year, several improvements have significantly reduced the uncertainties of the mercury UIMs. At higher pressures, the largest uncertainty for the UIMs had been due to the nonlinear propagation characteristics of the ultrasonic signal. A theoretical correction for this "diffraction" effect has been developed and tested experimentally. At the lowest pressures, the uncertainties are dominated by systematic nonlinearities in the phase detectors. An extension of the ultrasonic technique to include measurements with 50 or more frequencies limits these effects to the equivalent of 10 mPa. Inclusion of the diffraction correction, the multiple-frequency measurements, and an evaluation of several years of operating experience, has resulted in a one-sigma uncertainty due to systematic effects of 10 mPa + 2.6 parts per million (ppm). This is comparable to the uncertainty of the best pressure standards in the world; at low pressures, it is significantly better than any other published pressure standard.

Since the incorporation of the diffraction correction and other improvements, the UIM has been compared with two other national standards claiming "state-of-the-art" uncertainties, those in Germany and Slovakia. The results show agreement to within the one-sigma combined uncertainties of each pair of the three standards.

The diffraction correction has been applied to old NBS data on the speed of sound in mercury. This has resulted in a new value for the speed of sound at zero applied pressure and 23 °C of 1449.432 m/sec, which is 6.2 ppm less than the previous value.

Some UIM measurements are compromised by the vapor pressure of mercury, which is two orders of magnitude larger than the equivalent ultrasonic length resolution. To overcome that impediment and make full use of the ultrasonic technique at low pressures, a UIM has been developed that uses a low-vapor-pressure oil as the manometer fluid. This instrument has a full range of 100 Pa and a demonstrated stability of better than 1 mPa over a period of days.

## **18. Studies of Transition Range Flow Phenomena**

**J.P. Looney and S.A. Tison**

The accurate generation and understanding of a wide range of flows is important for the vacuum processing and equipment industries. In particular, transition flow is important in

the design of molecular-drag vacuum pumps, modeling and control of plasma and chemical-vapor-deposition semiconductor processing, vacuum-gage calibration, and vacuum-gage and system design. While theories for the extremes of molecular flow and viscous flow are well established, the theory for the transition from molecular to viscous flow is not; several empirical models exist, but they are valid only for simple geometries with small pressure gradients along the conductance element.

To understand the physical processes that govern transition flow, an experimental investigation of the flow through tubular elements has been undertaken. Tubular elements were chosen for three reasons: their common use as vacuum components and as leaks to admit gas into vacuum systems, the existence of empirical models describing their behavior for small pressure differentials, and their suitability for further theoretical modeling.

Some empirical models and references in the literature claim that for small pressure differences the conductance of a long tube will have a minimum in the transition region between molecular and viscous flow; other models do not predict such a minimum. Our experiments on a tube with a length-to-diameter ratio of 100 verified the existence of such a minimum over a wide range of pressure gradients. On the other hand, for orifices ("zero-length tubes"), first-order kinetic-theory models predict that the conductance increases linearly with increasing pressure in the transition regime. Our experiments confirmed this behaviour and found the value of the slope to be 0.07 times the ratio of the molecular mean free path to the orifice diameter. The contrast between the observed increase in the conductance of an orifice, and the decrease observed for a long tube in the same flow regime, suggests that intermediate-length tubes might have a constant conductance at pressures well above the molecular-flow regime. It was found that a tube with a length-to-diameter ratio of 1.9 maintains a constant conductance to within 0.1% to pressures a factor of 10 higher than where the same deviation occurs for orifices.

The data described above are being used to develop a robust empirical model for flows through tubes from molecular to viscous flow. These data can be used to evaluate the reliability of Monte Carlo codes used to calculate the flow conductances of other geometries.

## 19. Optical Measurements of Ultrahigh Vacuum Processes

**J.P. Looney and J. Kelley**

In a wide variety of applications, the measurement and control of contaminant gases such as H<sub>2</sub>O, CO, CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> can be critical to product yield, reliability, and process efficiency. The measurement of low number densities of these gases is often limited by perturbations of the vacuum environment by conventional vacuum instruments. To address this limitation, measurements have been undertaken to determine the feasibility of using laser spectroscopic techniques to provide a less intrusive probe of vacuum environments. The

current effort has focused on the use of resonance-enhanced multi-photon ionization coupled with time-of-flight mass spectroscopy (REMPI-TOF).

During the past year, experiments were conducted aimed at identifying the critical factors limiting this measurement approach. It was found that ultimate detection limits are highly species and optical-transition dependent, and sensitivities are strongly dependent on laser operating parameters such as focusing and beam alignment. However, when critical parameters were carefully controlled, and the system was calibrated at higher pressures, it was found that measurements of CO densities could be made with an accuracy of 10-15% and that an ultimate detection sensitivity of  $10^5$  molecules/cm<sup>3</sup> ( $10^{-10}$  Pa) could be achieved. The factors establishing this detection limit were photon-stimulated gas desorption from the chamber walls and components, and the random noise of the present measurement instrumentation. The CO measurements were unaffected by N<sub>2</sub> background pressures eight orders of magnitude higher, which is of significant importance for the detection of low-level contaminants in process environments. These results will appear shortly in the Journal of Vacuum Science and Technology.

Once the feasibility of the REMPI-TOF approach was established, it was used to study the interactions of conventional vacuum instruments with other gases. For instance, it was found that a conventional Bayard-Alpert type ionization gage, operating with a tungsten filament in an O<sub>2</sub> pressure of  $10^{-6}$  Pa, converts as much as 15% of the oxygen to CO. It appears that this process is limited by the rate at which carbon impurity atoms diffuse through to the surface of the tungsten filament.

Initial steps have been taken during this past year to evaluate a second optical technique -- infrared absorption. Prototype experiments using tunable diode lasers have identified several limiting noise sources in the laser and detectors. These depend upon laser operating parameters and on the mode of operation of the detector, e.g., photovoltaic vs. photoconductive mode. Experiments also were conducted to determine the relative sensitivities of various modulation schemes and the optimal modulation index and frequency for the different approaches. This work was complemented by theoretical modeling of the modulation waveforms and of the dependence of the signals on the modulation index and frequency.

## **20. Development of Improved Vacuum Instrumentation**

**P.J. Abbott, F.G. Long, J.P. Looney, D.R. Martin, A.P. Miiller, and C.R. Tilford**

Several years of experience calibrating vacuum gages submitted by industrial customers have shown that commercial glass-tubulated Bayard-Alpert gage tubes, when operated with certain types of control electronics, exhibit systematic non-linearities that are as large as 15-20% --

significantly exceeding reasonable limits for this type of instrument. A recent investigation has shown that this non-linearity was due to a pressure-dependent charging of the inner surface of the glass envelope, and that when the potential of the inner surface was fixed at the DC filament potential, the sensitivity of the gage remained constant to within 2% over the pressure range from  $10^{-7}$  to  $10^{-2}$  Pa. This pressure-dependent charging has been linked to the chopped-AC waveform used in these controllers to heat the gage filament. A minor modification of the electron-emission control circuitry should eliminate this nonlinear response and allow manufacturers to produce an improved product.

An effort has been undertaken to develop improved low-pressure (0.1 to 1000 Pa) transfer standards. This effort is supported by NASA-Langley to obtain the measurement accuracies required for their National Transonic Facility, as well as for other NASA applications. Two possible solutions are under investigation: (1) the development of a hybrid Capacitance Diaphragm Gage (CDG) that uses a thermoelectric module to provide improved temperature control for a commercial sensor, and (2) the development of a fused-quartz sensor and a three-terminal capacitance bridge readout. To date, a study of the measurement performance of commercial CDGs has been carried out to obtain baseline data on several key factors: zero instability, thermal transpiration, and response-function (calibration) shifts. A hybrid system has been assembled and tested. The results demonstrate significantly improved zero stability for the hybrid system and a minimization of thermal-transpiration effects when the temperature is controlled near room temperature. Replacement of the commercial electronic readout with a three-terminal capacitance bridge further improves the low-pressure performance by a factor of 4-5, but the performance is limited ultimately by other effects, probably mechanical instabilities in the commercial sensor. Fabrication of a fused-quartz sensor to replace the commercial sensor has been started.

Over the past three years, the Vacuum Group has been working on the design of a PC-based Spinning Rotor Gage (SRG) controller. During this past year, the design has been improved with the inclusion of a 16-bit data interface that will allow for the operation of up to four SRG controllers with one PC. Experiments have been completed recently which demonstrate that the use of the NIST SRG controllers allows operation at pressures that are a factor of 20 lower than are possible with the commercial controllers. Several control units have been produced for routine NIST use, and a publication that will allow commercial production of this instrument is in preparation.

## **21. Gas Evolution from Solids**

**S.A. Tison**

All materials evolve gas. Some of the gas originates as surface-adsorbed molecules, some is desorbed from the bulk. The rate of evolution is controlled by the surface binding energies and the bulk diffusion constants. In general, these processes have been studied because of

their importance in limiting the attainment of ultrahigh vacuum; they are also of interest in generating controlled flows of gas, e.g., as in standard leaks.

Earlier work concentrated on the diffusion properties of glasses, which are widely used for helium standard leaks. With a change in focus of the leak standards development effort towards refrigerant leaks, our interest has turned to the diffusion properties of polymers, particularly fluoropolymers. It has been found that diffusion rates of some of these materials are affected significantly by phase changes near room temperature. These phase changes are sample dependent and generally not noted in compilations of material properties. Apparently, the phase changes depend on the processing history of the material, and it appears possible to select materials that have a smooth temperature dependence over a usable range of temperatures. Experiments are currently underway to determine the effect of co-adsorbed molecules on the rate of evolution from the surface.

A different interest in adsorption-desorption phenomena is generated by the evidence that the kilogram has experienced a significant loss of mass, 50-100 micrograms, over the century since the establishment of the metric or SI system of units. One of the more plausible explanations for this change is the loss of absorbed hydrogen from the 90% platinum - 10% iridium cylinder that defines the kilogram. It is also well established that there are significant changes in the mass of standard kilograms in the days and weeks following cleaning. To understand the physical process of hydrogen adsorption and desorption, an experiment was conducted to determine the total mass of adsorbed gases on the surface and in the bulk of platinum and platinum-iridium alloys. It was determined that the equivalent of 1 monolayer of hydrogen was adsorbed on the surface of both platinum and a 90% platinum - 10% iridium alloy. Other adsorbed gases included 0.2 monolayers of carbon dioxide, 0.1 monolayer of carbon monoxide, and an undetermined amount of water. Additionally, 10 nanograms of hydrogen were absorbed in the bulk of a 1-gram platinum sample. Although this is less than the corresponding mass change of the kilogram, it should be noted that platinum processing techniques have changed significantly since the fabrication of the kilogram. The older techniques included a final melting of the alloy using the direct application of a hydrogen-oxygen flame, which could have increased the amount of bulk hydrogen significantly. The diffusivity was determined as a function of temperature from 200 to 800 °C. The average binding energy of hydrogen on the platinum could be determined from these data and compared to the binding energies on platinum with special surface treatments or on other metals, such as stainless steel.

## 22. Development of Gas-Operated Piston Gages as Primary Pressure Standards

C.D. Ehrlich, R.G. Driver, J.W. Schmidt, R.C. Veale (MEL), T.D. Doiron (MEL), J.R. Stoup (MEL), P. Delajoud (DH Instruments), M. Girard (DH Instruments), and K. Kurtz (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 NIST Pressure Group is working to develop such primary gas-operated deadweight piston gages through independent research activities, plus a Cooperative Research and Development Agreement (CRADA) with the NIST Dimensional Metrology Group (DMG) and DH Instruments, Inc.

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 50-mm diameter. The piston and cylinder are made of a ceramic material that provides good thermal expansivity, light weight for lower-pressure operation (down to 2.5 kPa), and good surface finish. The cylinder is the rotating element, and the gage is of a controlled-clearance design that operates in both the gage mode (atmospheric pressure above the piston) and the absolute mode (essentially vacuum above the piston).

Three sets of pistons/cylinders have been fabricated, tested for laboratory performance, and measured dimensionally. Initial performance tests revealed deficiencies that were easily remedied. Dimensional measurements showed these parts to be among the roundest ever seen by the NIST DMG. Furthermore, the newly acquired ability of the NIST DMG to perform roundness measurements with uncertainties of  $\pm 0.03$  micrometers, and diameter measurements on pistons and cylinders with uncertainties of  $\pm 0.06$  micrometers and  $\pm 0.07$  micrometers, respectively, yielded a nominal uncertainty in the dimensionally-measured effective area of the gage of 3 parts per million (ppm). Pressure measurements made with such a gage will have uncertainties that are highly competitive with measurements made by the best manometers. Possible additional uncertainties having to do with the adequacy of the model appear to be of the same magnitude but are still under investigation.

### 23. Progress Towards New High-Pressure Calibration Services

C.D. Ehrlich, S.W. Doty, D.B. Ward, and J. Houck

In response to customer inquiries, other-agency requests, and international interest, the NIST Pressure Group has begun efforts to increase the upper-end pressure for which calibration services are offered in both pneumatic and hydraulic media. Gas calibration services are being developed to the 100 MPa level, while the goal for oil calibration services is to go from the current 280 MPa maximum pressure to at least 500 MPa and possibly 700 MPa.

Recent advances in commercial gas-operated piston gage technology have brought to the market two different types of high pressure (~110 MPa, or 16,000 psi) gas gages from independent manufacturers. The designs of the two gages differ in that oil fills the gap between the piston and cylinder in one of the instruments but not the other. Two test benches are being developed to evaluate the potential of the two types of gages as useful transfer standards with acceptable levels of uncertainty.

One of the test benches is in place and has been used to investigate a method of effectively calibrating a gas test gage with an oil standard gage. The method involves using a directly visible liquid-gas interface (VLI) and a liquid-liquid differential pressure (DP) cell to separate the standard and test instruments in a traditional cross-float configuration. While this system has been used to provide a viable calibration, difficulties were encountered with this arrangement, including the gas dissolving in the oil, the lack of constancy of the oil level in the VLI, and the removal of trapped bubbles in the DP cell. Future plans include investigating the use of a DP cell as a fluid separator to avoid the problem of the gas going into solution.

For those applications where the presence of oil is undesirable or even hazardous, a test bench incorporating a gas-lubricated high-pressure piston gage is being developed wherein the oil can be eliminated completely from the customer calibration process. Characterization of the bench will include studies using both oil and gas standard piston gages. Calibration of customer gas gages by the gas-operated standard gage will include the use of a DP cell, or the removal of the DP cell entirely, with direct gas-gas communication between two gas-operated piston gages, using fall rate measurements to determine balance.

The need to provide calibration services for commercially-available hydraulic piston gages that operate to 500 MPa has prompted the Pressure Group to evaluate a prototype primary controlled-clearance piston gage at the White Sands Missile Range Facility. Early indications are that a gage of such a design may meet NIST's needs, and development may also lead to an improved theory of controlled-clearance piston gages.



## C. Outputs and Interactions (Thermophysics Division)

### 1. Publications

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## 2. Talks

- Berg, R.F., "The Oscillating Screen Viscometer for the Critical Viscosity Experiment," NASA Lewis Research Center, Cleveland, OH, October 27, 1992. Invited
- Berg, R.F., "Thermal Equilibration Near the Critical Point: Effects due to Three Dimensions and Gravity," Spring Meeting of the American Physical Society, Washington, DC, April 14, 1993.
- Berg, R.F., "Viscosity near the Critical Point: Mechanical Measurements on a Vibrating Space Shuttle," Department of Physics, University of Florida, Gainesville, FL, June 28, 1993. Invited
- Bruno, T.J., "Alternative Refrigerants as Supercritical Fluid Solvents," Eastern Analytical Symposium, Sommerset, NJ, November 17, 1992.
- Bruno, T.J., "Applications of the Vortex Tube in Chemical Analysis," Eastern Analytical Symposium, Sommerset, NJ, November 17, 1992.

- Bruno, T.J., "Outstanding Contributions in Chromatography by Daniel E. Martire," Eastern Analytical Symposium, Sommerset, NJ, November 18, 1992. Invited
- Bruno, T.J., "Measurements of Diffusivity in Supercritical Fluid Systems," Winter National Meeting, American Institute of Aeronautics and Astronautics, Reno, NV, January 14, 1993. Invited
- Bruno, T.J., "Standards in Process Analytical Chemistry," International Forum on Process Analytical Chemistry, Galveston, TX, January 27, 1993.
- Bruno, T.J., "Physical Properties of PCB's for Separation Design," Winter Meeting, Gas Research Institute, Boulder, CO, January 29, 1993. Invited
- Bruno, T.J., "Physicochemical and Instrumental Aspects of PCB Analysis in Natural Gas," AIChE 1993 Spring National Meeting, Houston, TX, March 31, 1993.
- Bruno, T.J., "Adsorption of PCB's on Surfaces," GRI PCB Task Force Meeting, Denver, CO, June 17, 1993. Invited
- Cezairliyan, A., "Measurement of Thermophysical Properties of Metals and Alloys at High Temperatures by Subsecond Pulse Heating Techniques," Workshop on Thermophysical Properties of Molten Materials, Cleveland, OH, October 22, 1992.
- Ehrlich, C.D., "Status of the NCSL Recommended Standards Practice on Deadweight Pressure Gauges," Measurement Science Conference, Anaheim, CA, January 22, 1993. Invited
- Ehrlich, C.D., "A Review of Gas-Operated Piston Gauges," CCM Second International Seminar on Pressure Metrology from 1 kPa to 1 GPa, Paris, France, June 2, 1993. Invited
- Ehrlich, C.D., "Elastic Distortions of a Multi-Mode Piston-Cylinder Unit up to 28 MPa," Joint AIRAPT/APS Conference, Colorado Springs, CO, June 30, 1993.
- Ehrlich, C.D., "Recent Advances in Pressure Measurement at NIST," 1993 NCSL Workshop and Symposium, Albuquerque, NM, July 26, 1993.
- Filippelli, A.R., "Linearity and Stability with Time and Use: Calibration Results for Two Commercial Extractor Ionization Gauges," IUVESTA Workshop on Ultra-High Vacuum Measurement, Grange-over-Sands, UK, October 7, 1992.

- Filippelli, A.R., "Linearity and Stability with Time and Use: Calibration Results for Two Commercial Quadrupole Partial Pressure Analyzers," Grange-over-Sands, UK, October 9, 1992.
- Friend, D.G., Huber, M.L., and Gallagher, J.S., "Thermophysical Property Computer Packages from NIST," ASME Winter Annual Meeting, Anaheim, CA, November 9, 1992.
- Friend, D.G. and Haynes, W.M., "Reference Data for the Thermophysical Properties of Fluids," AIChE 1993 Spring National Meeting, Houston, TX, March 31, 1993.
- Friend, D.G. and Rumble, J.R., "Standard Reference Data in Thermodynamics and Thermophysical Properties for Aerospace Applications," SAE Committee S-15, Meeting No. 28, Phoenix, AZ, April 1, 1993. Invited
- Friend D.G. and Haynes, W.M., "Properties of Ammonia-Water Mixtures," NREL Seminar, Golden, CO, June 27, 1993. Invited
- Friend, D.G., "Thermophysical Properties of Ammonia-Water Mixtures," IAPWS Working Group Report, Milan, Italy, September 13, 1993.
- Gillis, K.A., "Beyond CFC's: Can We Find Suitable Alternatives," Department of Physics, The Catholic University of America, Washington, DC, March 4, 1993. Invited
- Gillis, K.A., "Thermophysical Properties of Noble Gases and their Mixtures," Workshop on Thermoacoustic Research for Environmentally Safe Ships Program, Naval Postgraduate School, Monterey, CA, March 26, 1993. Invited
- Given, J.A., "Integral Equation Results for the Liquid-Gas Critical Point in a Fluid," Institute for Physical Science and Technology, University of Maryland, College Park, MD, February 12, 1993. Invited
- Given, J.A., "On the Renormalization Group in Liquid-State Theory," Institute for Physical Science and Technology, University of Maryland, College Park, MD, March 5, 1993. Invited
- Given, J.A., "An Integral Equation Theory for the Critical Region of a Fluid," Thermophysics Division Seminar, NIST, Boulder, CO, April 20, 1993.
- Given, J.A., "An Extended Corresponding States Model for Aqueous Mixtures," Thermophysics Division Seminar, NIST, Gaithersburg, MD, July 12, 1993.



- Hanley, H.J.M., "Thermophysical Property Research at NIST," Imperial College, London, United Kingdom, March 16, 1993.
- Hanley, H.J.M., "Neutron Scattering from Mixtures," Tech. Univ. of Berlin, Berlin, Germany, April 9, 1993.
- Haynes, W.M., "Experimental Measurements of Density for Natural Gas Liquids," Gas Processors Association 72nd Annual Convention, San Antonio, TX, March 15, 1993. Invited
- Haynes, W.M. and Friend, D.G., "Reference Data for the Thermophysical Properties of Cryogenic Fluids," Cryogenic Engineering Conference, Albuquerque, NM, July 14, 1993.
- Lettieri, T.R., "Investigation of Annular Forces Using an Oscillating, Gas-Operated Piston Gauge," Joint AIRAPT/APS Conference, Colorado Springs, CO, June 29, 1993.
- Looney, J.P., "The NIST Transition Range Standard," 12th International Vacuum Congress, The Hague, The Netherlands, October 14, 1992.
- Looney, J.P., "Optical Measurements of Low Gas Densities," Physikalisch-Technische Bundesanstalt (PTB), Berlin, Germany, October 20, 1992.
- Looney, J.P., "Optical Measurements of Low Gas Densities," KFA, Julich, October 21, 1992.
- Looney, J.P., "Optical Measurements of Low Gas Densities," Institute for Vacuum and Electronic Techniques (IEVT), Ljubljana, Slovenia, October 23, 1992.
- Looney, J.P., "Monte Carlo Calculations of Flow in the Transition Regime," 39th National Symposium, AVS, Chicago, IL, November 9, 1992.
- Looney, J.P., "Measurement of CO Pressures in the UHV Regime Using Resonance Enhanced Multiphoton Ionization Time of Flight Mass Spectroscopy," Sandia National Labs, Albuquerque, NM, May 7, 1993.
- McLinden, M.O., "Development of a Dual-Sinker Densimeter for High-Accuracy P-V-T Measurements," 11th Symposium on Energy Engineering Sciences, Argonne, IL, May 3, 1993.
- McLinden, M.O., "The REFPROP Thermodynamic Properties Database," Alternative Refrigerants Evaluation Program Meeting, Denver, CO, June 24, 1993. Invited

- McLinden, M.O., "The REFPROP Refrigerant Properties Database: Capabilities, Limitations, and Future Directions," ASHRAE/NIST Refrigerants Conference, Gaithersburg, MD, August 19, 1993. Invited
- Miiller, A.P., "Development of Improved Low Pressure Transfer Standards," 16th Annual NASA Metrology and Calibration Workshop, NIST, Gaithersburg, MD, April 21, 1993.
- Moldover, M.R., "Scientific Context of the Critical Viscosity Experiment," NASA Lewis Research Center, Cleveland, OH, October 27, 1992. Invited
- Moldover, M.R., "Acoustic and Microwave Resonances for Measuring Temperature and the Universal Gas Constant," Department of Chemistry, University of Maryland, College Park, MD, December 2, 1992. Invited
- Moldover, M.R., "Thermophysical Properties of Gases from Acoustical Measurements," Chemical Science and Technology Laboratory Colloquium, NIST, Gaithersburg, MD, February 10, 1993. Invited
- Moldover, M.R., "Dielectric Measurements Under Difficult Conditions," 11th Symposium on Energy Engineering Sciences, Argonne National Laboratory, Argonne, IL, May 4, 1993.
- Moldover, M.R., "Comparison of REFPROP 4.0 with Data," Alternative Refrigerants Evaluation Program Meeting, Denver, CO, June 25, 1993. Invited
- Mountain, R.D., "Simulation Studies of Nucleation and Growth," Gordon Research Conference on Crystal Growth, Oxnard, CA, March 15, 1993. Invited
- Mountain, R.D., "Simulation Studies of Crystal Nucleation and Growth," Thermophysics Division Seminar, NIST, Gaithersburg, MD, March 29, 1993.
- Mountain, R.D., "Supercooled Liquids," Department of Physics, Johns Hopkins University, Baltimore, MD, April 28, 1993. Invited
- Outcalt, S.L., "A Gas Chromatographic Detector for Hydrocarbons Based on Catalytic Cracking," AIChE 1993 Spring National Meeting, Houston, TX, March 31, 1993. Invited
- Pellegrino, J.J., "Towards Rational Pressure-Driven Standards," 1992 Membrane Planning and Technology Conference, Newton, MA, October 15, 1992.

- Pellegrino, J.J., "Gas Transport Properties of Solution-Cast PFSA with Surfactants," AIChE 1992 Fall National Meeting, Miami, FL, November 6, 1992.
- Pellegrino, J.J., "Gas Transport Properties of Solution Cast Polyperfluorosulfonic Acid Ionomer Films Containing Ionic Surfactants," International Membrane Science and Technology Conference 1992, Sydney, Australia, November 13, 1992.
- Pellegrino, J.J., "Chitin and Chitosan: New Importance for Old Materials in Separations," Risk Reduction Engineering Laboratory, EPA, Cincinnati, OH, January 27, 1993. Invited
- Pellegrino, J.J., "Principles of Membrane Separations," Shortcourse: Interagency Consortium for Desalination and Membrane Separation Research, Keystone, CO, April 28, 1993. Invited
- Pellegrino, J.J., "Determination of Total Protein Adsorbed on Solid (Membrane) Surface: Single Protein Adsorption," 6th American Filtration Society Meeting and Exposition, Chicago, IL, May 4, 1993.
- Pellegrino, J.J., "Membrane Gas Separation for Fluidized-Bed Incinerator: Why, What, and Lab Tests," 6th American Filtration Society Meeting and Exposition, Chicago, IL, May 4, 1993.
- Pellegrino, J.J., "Gas Separations using Membranes," Los Alamos National Laboratory, Los Alamos, NM, July 16, 1993. Invited
- Pellegrino, J.J., "Polyperfluorosulfonate Ionomer Nafion - Function and Form," Los Alamos National Laboratory, Los Alamos, NM, July 16, 1993. Invited
- Pellegrino, J.J., "Continuous Electrophoretic Liquid Membrane Extraction of Aqueous Solutes," AIChE 1993 Summer National Meeting, Seattle, WA, August 18, 1993.
- Perkins, R.A., "Thermal Conductivity of New Refrigerants Over Wide Ranges of Temperature and Pressure," Workshop on Thermophysical Properties of Environmentally Acceptable Refrigerants, Ericeira, Portugal, November 19, 1992. Invited
- Perkins, R.A., "Further Adventures in Transient Hot-Wire Studies of Refrigerants," IUPAC Commission I.2: Thermodynamics - Transport Properties Subcommittee Meeting, Lisbon, Portugal, August 29, 1993.

- Perkins, R.A., "Thermal Conductivity of Pentafluoroethane (R125) from 190 to 390 K at Pressures to 70 MPa," 13th European Conference on Thermophysical Properties, Lisbon, Portugal, September 3, 1993.
- Peskin, A.P. and Hardin, G.R., "An Object-Oriented Programming Approach to Numerical Modeling of Chemical Vapor Deposition," AIChE 1992 Fall National Meeting, Miami, FL, November 13, 1992.
- Rainwater, J.C., "Liquid-Liquid and Liquid-Vapor Phase Changes in Mixtures," University of Colorado, Denver, CO, November 20, 1992. Invited
- Rainwater, J.C. and Friend, D.G., "Isothermal Vapor-Liquid Enthalpy Difference of Near-Critical Binary Mixtures," AIChE 1993 Spring National Meeting, Houston, TX, March 30, 1993.
- Rainwater, J.C., "Progress on a Nonclassical Model of Mixtures with Vapor-Liquid and Liquid-Liquid Equilibrium," Midwest Thermodynamics Symposium, Houghton, MI, May 24, 1993.
- Schmidt, J.W., "Gas and Mode, Vertical and Rotational Effects with a Three Piston Gauge Apparatus," CCM Second International Seminar on Pressure Metrology from 1 kPa to 1 GPa, Paris, France, June 2, 1993.
- Sengers, J.M.H. Levelt, "Supercritical Steam: Energy, Environment, Science", NIST Colloquium, Gaithersburg, MD, October 9, 1992. Invited
- Sengers, J.M.H. Levelt, "Congruence - An Accurate Property Estimator for Mixtures of Long n-Alkanes?," AIChE 1992 Fall National Meeting, Miami, FL, November 2, 1992.
- Sengers, J.M.H. Levelt, "Critical Behavior of Ionic Fluids," 68th Statistical Mechanics Meeting, Rutgers, NJ, December 18, 1992. Invited
- Sengers, J.M.H. Levelt, "The Science of Supercritical Steam: Application to Hazardous Waste Destruction," Thirteenth Annual Herzfeld Lecture, Department of Physics, The Catholic University of America, Washington, DC, February 18, 1993. Invited
- Sengers, J.M.H. Levelt, "Supercritical Water Oxidation for Environmental Cleanup," Department of Chemistry, Howard University, Washington, DC, March 12, 1993. Invited
- Sengers, J.M.H. Levelt, "Supercritical Water Oxidation," 13th Experimental Thermodynamics Conference, Bristol, UK, March 25, 1993. Invited

- Sengers, J.M.H. Levelt, "Theory and Experiment near the Critical Point," The Statistical Mechanics of Fluids Meeting, Physical Chemistry Laboratory, Oxford, UK, March 30, 1993. Invited
- Sengers, J.M.H. Levelt, "Critical Behavior of Fluids, Concepts and Applications. Part I. Basic Concepts," NATO ASI on Supercritical Fluids, Kemer, Antalya, Turkey, July 22, 1993. Invited
- Sengers, J.M.H. Levelt, "Critical Behavior of Ionic Fluids," Second Liquids Conference of the European Physical Society, Florence, Italy, September 21, 1993. Invited
- Sengers, J.M.H. Levelt, "Raman Spectroscopy and Thermodynamic Modeling Related to Supercritical Water Oxidation," IAPWS Meeting, Milan, Italy, September 14, 1993. Invited
- Sengers, J.V., "Critical Fluctuations and Classical Equations of State with Application to R134a," Workshop on Thermophysical Properties of Environmentally Acceptable Refrigerants, Ericeira, Portugal, November 19, 1992. Invited
- Sengers, J.V., "The Thermal Conductivity of R134a," Workshop on Thermophysical Properties of Environmentally Acceptable Refrigerants, Ericeira, Portugal, November 20, 1992. Invited
- Sengers, J.V., "Non-equilibrium Fluctuations in Dissipative Liquid Systems," Thermophysics Division Seminar, NIST, Gaithersburg, MD, March 8, 1993. Invited
- Sengers, J.V., "Effects of Critical Fluctuations on the Equation of State of Fluids and Fluid Mixtures," 13th Experimental Thermodynamics Conference, Bristol, UK, March 24, 1993.
- Sengers, J.V., "Transport Properties of Supercritical Fluids," NATO Advanced Study Institute on Supercritical Fluids, Kemer, Antalya, Turkey, July 18, 1993. Invited
- Sengers, J.V., "Thermodynamic Properties of Supercritical Fluids," NATO Advanced Study Institute on Supercritical Fluids, Kemer, Antalya, Turkey, July 19, 1993. Invited
- Tilford, C.R., "Can Partial Pressure Analyzers be Calibrated?," IUVSTA Workshop on Ultra High Vacuum Measurements, Grange-over-Sands, UK, October 9, 1992. Invited
- Tilford, C.R., "High Vacuum Water Primary Standards," 12th International Vacuum Congress, The Hague, The Netherlands, October 13, 1992.

- Tilford, C.R., "Vacuum Standards at NIST," Physikalisch-Technische Bundesanstalt (PTB), Berlin, Germany, October 20, 1992. Invited
- Tilford, C.R., "Vacuum Measurements Research at NIST," Austrian Research Center, Seibersdorf, Austria, October 23, 1992. Invited
- Tilford, C.R., "More Water; Further Results Calibrating Vacuum Instrumentation with Water," 39th National Symposium, AVS, Chicago, IL, November 11, 1992.
- Tilford, C.R., "Vacuum Gaging; Instruments and Techniques," Seventh Latin American Symposium on Surface Physics, Bariloche, Argentina, November 17, 1992. Invited
- Tilford, C.R., "Characteristics of Partial Pressure Analyzers," Seventh Latin American Symposium on Surface Physics, Bariloche, Argentina, November 19, 1992. Invited
- Tilford, C.R., "Low Pressure and Vacuum Standards at NIST," Physics and Metrology Branch of the Instituto Nacional de Tecnologia Industrial, Buenos Aires, Argentina, November 23, 1992. Invited
- Tilford, C.R., "Vacuum Gaging and Calibrations," Postec University, Pohang, Korea, January 6, 1993. Invited
- Tilford, C.R., "Vacuum and Leak Standards at NIST," Korean Research Institute of Standards and Science, Taejon, Korea, January 8, 1993. Invited
- Tilford, C.R., "New Developments at NIST in Vacuum, Low-Pressure, and Leak Standards," 16th Annual NASA Metrology and Calibration Workshop, Gaithersburg, MD, April 20, 1993.
- Tilford, C.R., "Three and a Half Centuries Later - The Modern Art of Liquid-Column Manometry," CCM Second International Seminar on Pressure Metrology from 1 kPa to 1 GPa, Paris, France, June 2, 1993. Invited
- Tilford, C.R., "The Current Status of Ultrasonic Manometry," CCM Second International Seminar on Pressure Metrology from 1 kPa to 1 GPa, Paris, France, June 3, 1993.
- Tilford, C.R., "Low-Pressure Effective Areas of a Gas-Operated Variable-Clearance Piston Gage," CCM Second International Seminar on Pressure Metrology from 1 kPa to 1 GPa, Paris, France, June 4, 1993.
- Tison, S.A., "Experimental Data and Theoretical Modeling of Gas Flows Through Metal Capillary Tubes," 12th International Vacuum Congress, The Hague, The Netherlands, October 15, 1992.

- Tison, S.A., "Hydrogen Adsorption and Desorption in Platinum," Bureau International des Poids et Mesures, Paris, France, October 19, 1992. Invited
- Tison, S.A., "Hydrogen Adsorption and Desorption in Platinum," Istituto di Metrologia G. Colonnetti, Turin, Italy, October 23, 1992. Invited
- Tison, S.A., "Revisiting Flow Phenomena in the Transition Flow Range," 39th National Symposium, AVS, Chicago, IL, November 9, 1992.
- Tison, S.A., "Calibration of Helium Leak Detectors for Quantitative Leak Rate Measurements," American Society of Non-Destructive Testing, 1992 Fall Conference, Chicago, IL, November 18, 1992.
- Tison, S.A., "New Development in Leak Calibration," Measurement Science Conference, Anaheim, CA, January 22, 1993.
- Tison, S.A., "Low-Density Water Vapor Measurements: The NIST Primary Standard and Instrument Response," RL/NIST Workshop on Moisture Measurement and Control for Microelectronics, April 5, 1993.
- Weber, L.A., "Effects of Dissolved Volatile Impurities on Thermophysical Properties Calculations for Refrigerants," Thermophysics Division Seminar, NIST, Boulder, CO, January 5, 1993.
- Weber, L.A., "Estimating the Virial Coefficients of the New Candidate Refrigerants and Their Mixtures," 13th European Conference on Thermophysical Properties, Lisbon, Portugal, September 2, 1993.

### **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)

### **4. Patent Awards and Applications**

Bruno, T.J., "Sample Cell for Infrared Spectrophotometry," Patent No. 5,217,904 (awarded June, 1993)

Looney, J.P., Long, F., and Tilford, C., "PC-Based Spinning Rotor Gauge Controller" (Submitted February 1993)

Pellegrino, J., "Enhancing Performance of Perfluorinated Ionomer Membranes via Dopant Incorporation" (Submitted February 1993)

5. SRM Activities

None

6. SRD Activities

SRD 4 NIST Thermophysical Properties of Hydrocarbon Mixtures Database, Support  
SRD 10 NIST Thermophysical Properties of Water Database, Support  
SRD 12 NIST Thermophysical Properties of Pure Fluids Database, Upgrade, Support  
SRD 14 NIST Mixture Properties Program Database, Upgrade, Support  
SRD 23 NIST Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Database (REFPROP), Upgrade, Support

7. Calibrations

Calibration services (pressure, vacuum, and leak rate) have been provided for the following organizations:

Air Force Newark	Litton Systems Inc.
Ametek Inc.	Lockheed Eng & Sciences Co.
Ball Aerospace Systems Group	Lockheed Missiles & Space Co.
Center for Measurement Stds	Ltv Aerospace & Defense
Consumers Power Co.	MKS Instruments Inc.
Csiro Div of Applied Physics	Martin Marietta Corp.
DH Instruments Inc.	Martin Marietta Energy Sys.
EG&G Chandler Engineering	Maryland Dept of Agriculture
EG&G Energy Measurements	McDonnell Douglas Corp.
Eastman Kodak Co.	NASA KSC
Edwards High Vacuum Intl	NASA Langley Research Center
GE Aerospace	Naval Weapons Station
GTE/ERS	Navy Primary Stds Lab West
General Dynamics	PSE&G
General Electric Aircraft	Rockwell International
General Electric Co.	Ruska Instrument Corp
Granville-Phillips Co.	Sandia National Labs
Honeywell Inc	TRW Space & Defense Sector
Johnson Controls World Svcs	Tracor Aerospace Inc.



US Army TMDE Activity  
Unified Industries Inc.  
Vacuum Technology Inc.  
Vaisala OY  
Varian Associates Inc.  
Veeco Instruments Inc.  
Vought Aircraft Co.  
Westinghouse Savannah River Co.  
Willson Scientific Glass Inc.

## 8. Committee Assignments

### **T.J. Bruno**

International Forum on Process Analytical Chemistry (Member, Scientific Board,  
ASTM Committee D03 on Gaseous Fuels  
PCB Task Force, GRI (Member)

### **A. Cezairliyan**

International Organizing Committee, European Thermophysical Properties Conference  
ASME K-7 Thermophysical Properties Committee  
International Thermophysics Congress (Chair)  
International Commission on Standardization of Thermophysical Measurement  
Techniques  
ASTM Thermophysical Properties Subcommittee  
International Organizing Committee of the Subsecond Thermophysics Workshops

### **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 Vacuum Technology Division (Board of Directors)  
AVS Recommended Practices Committee on the Calibration of Mass Spectrometers  
for Partial Pressure Analysis  
Journal of Vacuum Science and Technology Shop Note Award Committee (Chair)

**D.G. Friend**

Director, Fluid Properties Data Center  
International Association for Properties of Water and Steam, Working Group on  
Thermophysical Properties

**J.S. Gallagher**

International Association for Properties of Water and Steam, Working Group on  
Thermophysical Properties  
ASME Research and Technology Committee on Water in Thermal Power Systems  
ASME Research Subcommittee on the Properties of Water and Steam (Secretary)  
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

**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)

**M.L. Huber**

Boulder Editorial Review Board

**R.W. Hyland**

AVS Recommended Practices Committee on the Use of Capacitance Diaphragm  
Gages

**T.R. Lettieri**

Optical Society of America Education Council

**R.A. MacDonald**

Washington Editorial Review Board

**M.O. McLinden**

ASHRAE Technical Committee 3.1 - Refrigerants and Brines (Corresponding  
Member)  
ASHRAE Standards Project Committee 34 - Nomenclature and Safety Classification  
of Refrigerants  
International Energy Agency Annex 18 - Thermophysical Properties of  
Environmentally Acceptable Refrigerants (Operating Agent/Chair)

**A.P. Miller**

ASME K-7 Thermophysical Properties Committee  
ASTM Committee E37 on Thermal Measurements  
ASTM Thermophysical Properties Subcommittee  
Touloukian Award Subcommittee of the ASME Heat Transfer Division

**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 Separation 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

**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  
International Association for Properties of Water and Steam, Working Group on  
Physical Chemistry of Aqueous Systems  
ASME Research Committee on the Properties of Water and Steam in Thermal Power  
Systems  
12th Symposium on Thermophysical Properties, Program Committee (Chair)  
Advisory Committee of the Chemistry Division, Oak Ridge National Laboratory

**J.V. Sengers**

ASME K-7 Thermophysical Properties Committee  
ASME Research Committee on the Properties of Water and Steam in Thermal Power  
Systems  
International Association for Properties of Water and Steam, Working Group on  
Thermophysical Properties  
12th International Conference on the Properties of Water and Steam, Program  
Committee (Chair)  
Touloukian Award Subcommittee of the ASME Heat Transfer Division

**C.R. Tilford**

Radio and Technical Commission for Aeronautics, Special Committee 150,  
Performance Requirements for 100 Foot Vertical Separation of Aircraft Above  
Flight Level 290

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**

American Laboratory (Guest Editor)

**A. Cezairliyan**

Compendium on Thermophysical Properties Measurement Methods, Plenum  
Publishing Company (Editor)

International Journal of Thermophysics (Editor-in-Chief)

Journal of High Temperature Science (Editorial Board)

High Temperatures-High Pressures (Editorial Board)

**H.J.M. Hanley**

International Journal of Thermophysics (Editorial Board)

**J.J. Pellegrino**

Gas Separation and Purification (Editorial Board)

**J.V. Sengers and W.A. Wakeham**

International Journal of Thermophysics, Volume 14, pp. 613-992 (1993), special issue  
in honor of Joseph Kestin

**C.R. Tilford**

Vacuum (Editorial Board)

## 10. Seminars

### October 2, 1992

Dr. Benjamin R. Mattes, Los Alamos National Laboratory, Los Alamos, NM, "Polyaniline Membranes for Gas Separations." (Division Sponsor: T.J. Bruno)

### December 16, 1992

Dipl.-Ing Torsten Luddecke, Institute of Thermodynamics, University of Hanover, Hanover, Germany, "Structural Optimization, A Statistical Method for Correlating Equations." (Division Sponsor: J.W. Magee)

### January 4, 1993

Dr. David T. Croft, Department of Chemical Engineering, University of Virginia, Charlottesville, VA, "Direct Determination and Multiplicity of Periodic States of Adsorption Cycles." (Division Sponsor: M.R. Moldover)

### January 7, 1993

Dr. Lloyd A. Weber, Thermophysics Division, NIST, Gaithersburg, MD, "Determining Thermodynamic Properties of the New Refrigerants at Low Reduced Temperatures, Some Problems and Their Solutions." (Division Sponsor: W.M. Haynes)

### February 8, 1993

Professor Jan V. Sengers, Institute for Physical Science and Technology, University of Maryland, College Park, MD, "Non-Equilibrium Fluctuations in Dissipative Liquid Systems." (Division Sponsor: M.R. Moldover)

### February 22, 1993

Professor Sergei B. Kiselev, Physics Department, Moscow Gubkin Oil and Gas Research Institute, Moscow, Russia, "Global Critical Phenomena in Fluids and Fluid Mixtures: Application to Methane and Ethane." (Division Sponsor: J.C. Rainwater)

### March 8, 1993

Professor Jan V. Sengers, Institute for Physical Science and Technology, University of Maryland, College Park, MD, "Effect of Critical Fluctuations on the Equation of State of Fluids and Fluid Mixtures." (Division Sponsor: M.R. Moldover)

### April 5, 1993

Dr. Yong Soo Kang, Korean Institute for Science and Technology, Seoul, Korea, "Analysis of Mass Transport Through Three-Phase System." (Division Sponsor: J.J. Pellegrino)

**April 14, 1993**

Dr. James A. Given, Thermophysics Division, NIST, Gaithersburg, MD, "An Integral Equation Theory for the Critical Region of a Fluid." (Division Sponsor: D.G. Friend)

**May 10, 1993**

Professor James B. Mehl, Department of Physics, University of Delaware, Newark, DE, "Acoustic Viscometer: Review of Theoretical Modeling and Experimental Work in Air." (Division Sponsor: M.R. Moldover)

**June 9, 1993**

Professor G.M. Schneider, Ruhr Universitat Bochum, Lehrstuhl fur Physikalische Chemie II, Bochum, Germany, "Physicochemical Principles and Applications of Supercritical Fluid Chromatography." (Division Sponsor: J.M.H. Levelt Sengers)

**July 23, 1993**

Kenneth N. Marsh, Thermodynamics Research Center, The Texas A&M University System, College Station, TX, "Towards a World Data Depository on Thermophysical Properties." (Division Sponsor: W.M. Haynes)

**August 16, 1993**

Professor Noboru Kagawa, Department of Applied Physics, The National Defense Academy, Yokosuka, Japan, "Stirling Engine Heat Pumps." (Division Sponsor: W.M. Haynes)

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

**November 18, 1992**

Eastern Analytical Symposium Award in Chromatography, Presented to Daniel E. Martire; Special Session, Eastern Analytical Symposium, Sommerset, NJ (T.J. Bruno).

**January 26, 1993**

Standards in Process Analytical Chemistry, Special Session, International Forum on Process Analytical Chemistry, Galveston, TX (T.J. Bruno).

**January 27, 1993**

Process Environmental Analysis, Special Session, International Forum on Process Analytical Chemistry, Galveston, TX (T.J. Bruno).

**March 28 - April 1, 1993**

Analytical Measurements I: Gas Industry, Analytical Measurements II: Petrochemical Industry, Analytical Measurements III: Sampling and Data Analysis, AIChE 1993 Spring National Meeting, Houston, TX (T.J. Bruno).

**July 19-30, 1993**

NATO Advanced Summer Institute on Supercritical Fluids, Kemer, Antalya, Turkey (J.M.H. Levelt Sengers)

## VIII. Glossary

### Government Agencies and Departments

ADAMHA	Alcohol, Drug Abuse, and Mental Health Administration
AFB	Air Force Base
AFOSR	Air Force Office of Scientific Research
AFTAC	Air Force Technical Applications Center
ARPA	Advanced Research Projects Agency
ATP	Advanced Technology Program
BFRL	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
JANNAF	Joint Army-Navy-National Aeronautics and Space Administration-Air Force Data Evaluation Project
LANL	Los Alamos National Laboratory
MEL	Manufacturing Engineering Laboratory
MRG	Microanalysis Research Group
MSEL	Materials Science and Engineering Laboratory
NASA	National Aeronautics and Space Administration
NAVSSSES	Naval Ship Systems Engineering Station
NBS	National Bureau of Standards
NBSB	National Biomonitoring Specimen Bank
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
NOAA	National Oceanic and Atmospheric Administration



NRL	Naval Research Laboratory
NSF	National Science Foundation
OARD	Organic Analytical Research Division
ORNL	Oak Ridge National Laboratory
RSA	Republic of South Africa
RTI	Research Triangle Institute
SRDP	NIST Standard Reference Data Program
USDA	Department of Agriculture
USN/CCG	U.S. Navy/Calibration Coordination Group
WHOI	Woods Hole Oceanographic Institute
WRDC	Wright Research and Development Center

### Foreign Standards Laboratories

CENAM	Centro Nacional de Metrologia (Mexico)
CCT	Comite Consultatif de Thermometrie
CIPM	Comite International des Poids et Mesures
CMS/ITRI	Center for Measurement Standards/Industrial Technology Research Institute (Taiwan)
IMEKO	International Measurement Congress
IMGC	Instituto di Metrologia "G. Colennetti" (Italy)
INSA de Rouen	l'Institut Nationale Scientifique Appliquee (Rouen France)
NRC	National Research Council of Canada
NRLM	National Research Laboratory of Metrology (Japan)
PTB	Physikalisch-Technische Bundesanstalt (Germany)
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
ANSI	American National Standards Institute
API	American Petroleum Institute
APS	American Physical Society
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
ATP	Advanced Technology Program
BIPM	International Bureau of Weights and Measures
BRS	Biotechnology Research Subcommittee
CAALS	Consortium on Automated Analytical Systems
CAL	California Institute of Technology
CAP	College of American Pathologists
CARB	Center for Advanced Research in Biotechnology
CIPM	International Committee of Weights and Measures
CLSH	Committee on Life Science and Health
CONEG	Coalition of Northeastern Governors
CPAC	Consortium on Process Analytical Chemistry
CRC	Chemical Rubber Company
CSIRO	Commonwealth Scientific and Industrial Research Organization
DIPPR	Design Institute for Physical Property 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
IAEA	International Atomic Energy Agency
IAPWS	International Association for the Properties of Water and Steam
ICUMSA	International Commission for Uniform Method of Sugar Analysis
IEA	International Energy Agency
IEC	International Electrotechnic Commission
IEEE	Institute of Electronic and Electrical Engineers
ILASS	Institute for Liquid Atomization and Spray Systems
IPMI	International Precious Metals Institute
IRMM	Institute for Reference Materials and Measurements
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
NCCLS	National Clinical Chemistry Laboratory Standards
NCSL	National Conference of Standards Laboratories
NDRL	Notre Dame Radiation Laboratory
SEMATECH	Semiconductor Industry Technology Consortium
SPIE	Society of Photo-optical Instrumentation Engineers
SWRI	Southwest Research Institute
TWGDAM	Technical Working Group on DNA Analysis Method

VAMAS  
WHO

Versailles Project on Advanced Materials and Standards  
World Health Organization

Technical

1D	One Dimensional
2D	Two Dimensional
AEM	Analytical Electron Microscope
AES	Auger-electron Spectroscopy
AFM	Atomic Force Microscope
AL	Attenuation Length
$\alpha$ -TNF	Antiproliferative Agents Tumor Necrosis Factor
AMP	Adenosine Monophosphate
AMS	Accelerator Mass Spectrometry
amu	Atomic Mass Unit
ANN	Artificial Neural Networks
ANS	Advanced Neutron Source
AP	Alkaline Phosphatase
ASCII	American Standard Computer Information Interchange
ASEM	Automated Scanning Electron Microscopy/Electron Probe Microscope
BASIC	Beginner's All-Purpose Symbolic Instruction Code
BMCD	Biological Macromolecule Crystallization Database
BR	Bacteriorhodopsin
BSA	Bovine Serum Albumin
C18	Octadecylsilane
CA	Carbonic Anhydrase
cAMP	Cyclic Adenosine Monophosphate
CBWA	Chemical/Biological Warfare Agents
CCP	Cytochrome c Peroxidase
CD-ROM	Compact Disk - Read-Only-Memory
CDG	Capacitance Diaphragm Gage
CE	Capillary Electrophoresis
CEM	Continuous Emission Monitoring
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 Activation Analysis
CNRF	Cold Neutron Reactor Facility

CO-Hb	Carbon Monoxide-hemoglobin
COSY	Correlation Spectroscopy Experiment
CPA	Carboxypeptidase A
CRADA	Cooperative Research and Development Agreement
CRP	Cyclic AMP Receptor Protein
CRT	Cathode Ray Tube
CSD	Carnahan-Starling-Desantis Equation of State
CSDM	Carnahan-Starling-Desantis-Morrison Equation of State
CVD	Chemical Vapor Deposition
DC	Direct Current
DCGD	Direct Current Glow Discharge
DDE	Dynamic Data Exchange
DFWM	Degenerate Four-wave Mixing
dL	Deciliter (10 <sup>-1</sup> liters)
DLS	Dynamic Light Scattering
DNA	Deoxyribonucleic Acid
DNB	Dinitrobenzene
DP	Differential-Pressure Cell
DSC	Differential Scanning Calorimetry
DTSA	Desktop Spectrum Analyzer
ECL	Electrogenerated Chemiluminescence
ECS	Extended Corresponding States
EDS	Energy Dispersive Spectrometer
EDTA	Ethylene-Diamine-Tetra-Acetic Acid
EMPA	Electron Probe X-ray Microanalysis
ESEM	Environmental Scanning Electron Microscopy
ESI-MS	Electrospray Ionization Mass Spectrometry
FAES	Flame Atomic Emission Spectrometry
FCTS	Flow Calibration Test Stand
FE-STEM	Field Emission-Scanning Transmission Electron Microscope
FIA	Flow Injection Analysis
FIIA	Flow Injection Immunoassay
FT	Fourier Transform
FTIR	Fourier Transform Infrared Spectrometry
FTS	Fourier Transform Spectrometer
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
GLMT	Generalized Lorenz-Mie Theory
GRT	Germanium Resistance Thermometers

GST	Glutathione-S-Transferase
H	Hydrogen
HCFC	Hydrochlorofluorocarbon
HDL	High Density Lipoproteins
HETCOR	Hetero Nuclear Correlation
HFC	Hydrofluorocarbon
HMBC	Hetero Nuclear Multiple Bond Correlation
HMQC	Hetero Nuclear Multiple Quantum Correlation
HPEC	High Performance Exclusion Chromatography
HSA	Human Serum Albumin
HTSPRT	High Temperature Standard Platinum Resistance Thermometer
HVAC	Heating Ventilation and Air Conditioning
Hb	Hemoglobin
ICP	Inductively Coupled Plasma
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ID-TIMS	Isotope Dilution Thermal Ionization Mass Spectrometry
IDMS	Isotope Dilution Mass Spectrometry
IFN-	Interferon-gamma
IMFP	Inelastic Mean Free Path
INAA	Instrumental Neutron Activation Analysis
IR	InfraRed
ITS-90	International Temperature Scale of 1990
IgG	ImmunoglobulinG
JP8	Designation for Jet Fuel
KHP	Potassium Hydrogen Phthalate
KIVA-II	Computational Fluid Dynamics Computer Code
LADH	Liver Alcohol Dehydrogenase
LC	Liquid Chromatography
LDH	Lactate Dehydrogenase
LDL	Low Density Lipoproteins
LDV	Laser Doppler Velocimetry
LEED	Low Energy Electron Diffraction
LEI	Laser-enhanced Ionization
LEI-MS	Laser-enhanced Ionization Mass Spectrometry
LIF	Laser-induced Fluorescence
LISP	List Processing Computer Language
LLE	Liquid-Liquid Equilibrium
LOX	Liquid Oxygen
LTE	Local Thermodynamic Equilibrium
Lp(a)	Lipoprotein (a)
MBE	Molecular Beam Epitaxy
MBWR	Modified Benedict-Webb-Rubin Equation of State

MD	Molecular Dynamics
MECE	Micellar Electrokinetic Capillary Electrophoresis
MFC	Mass Flow Controller
mg	Milligram (10 <sup>-3</sup> grams)
MHz	Megahertz
mL	Milliliter
MLx	MacLispix Image Processing Software
MRF	Metering Research Facility
MS	Mass Spectrometry
MW	Molecular Weight
NAA	Neutron Activation Analysis
NDP	Neutron Depth Profiling
NMR	Nuclear Magnetic Resonance
NSB	Non-specific Binding
NVLAP	National Voluntary Laboratory Accreditation Program
OES	Optical Emission Spectrometry
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
pH	Measure of the Concentration of Hydrogen Ions
PHA	Pulse-height Analyzer
PIV	Particle Image Velocimetry
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
ppbV	Parts-Per-Billion Volume
ppm	Part Per Million
ppmV	Parts-Per-Million Volume
PTS	Phosphotransferase System
PVT	Pressure-Volume-Temperature
PVTx	Pressure-Volume-Temperature-Composition
Rabc	Refrigerant abc
RDA	Recommended Dietary Allowance
REFPROP	NIST Computer Package for the Properties of Alternative Refrigerants

REGEN3.1	Computational Code for Cryocooler Modeling
REMPI	Resonance-Enhanced Multiphoton Ionization
rf	Radio Frequency
RFGD	Radio Frequency Glow Discharge
RFLP	Restriction Fragment Length Polymorphism
RHEED	Reflection High-energy Electron Diffraction
RIA	Radio Immunoassay
RIMS	Resonance Ionization Mass Spectrometry
RIRT	Rhodium/Iron Resistance Thermometer
RIS	Resonance Ionization Spectroscopy
RNA	Ribonucleic Acid
RNAA	Radiochemical Neutron Activation Analysis
RRKM	Unimolecular Reaction Rate Theory
RSC	Robotic Sample Changer
RSD	Relative Standard Deviation
RSF	Relative Sensitivity Factors
SAM	Self-Assembled Monolayers
SANS	Small Angle Neutron Scattering
SCCM	Standard Cubic Centimeters Per Minute
SCW	Supercritical Water
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
SI	International System of Units
SI	Semi-insulating
SIGMA	Supersonic Inert-Gas Metal Atomization
SIMS	Secondary Ion Mass Spectrometry
SLM	Standard Laboratory Module
SNR	Signal-to-Noise Ratio
SPC	Statistical Process Control
SPR	Surface Plasmon Resonance
SPRT	Standard Platinum Resistance Thermometer
SRD	Standard Reference Data
SRG	Spinning Rotor Gage
SRM	Standard Reference Material
SRP	Standard Reference Photometer
SSME	Space Shuttle Main Engine
STM	Scanning Tunnelling Microscope
SURF	Synchrotron Users Ultraviolet Radiation Facility
TADOPT	Thermoacoustically Driven Orifice Pulse Tube Refrigerator

TC	Thermocouple
TCA	Trichloroethane
TCP-IP	Transmission Control Protocol-Internet Protocol
TEA	Triethylamine
TFTC	Thin Film Thermocouple
TG	Triglycerides
THERM/EST	Name of Database Product
TIMS	Thermal Ionization Mass Spectrometry
TLD	Thermal Luminescence Dosimetry
TLN	Thermolysin
TN	Thermal Neutron
TNPGAA	Thermal Neutron Prompt Gamma Activation Analysis
TOCSY	Totally Correlated Spectroscopy
TOF	Time-of-Flight
TOF-SIMS	Time-of-Flight Secondary Ion Mass Spectrometer
TQM	Total Quality Management
Tc	Critical Temperature
Trp	Tryptophan
Try	Tyrosine
UIM	Ultrasonic Interferometer Manometer
UV	Ultraviolet
UV-VIS	Ultraviolet-Visible (Spectroscopy)
VLE	Vapor-Liquid Equilibrium
VLI	Vapor-Liquid Interface
VOC	Volatile Organic Compounds
VRD	Video Radiation Detector
WDS	Wavelength-dispersive X-ray Spectrometry
XOS	X-ray Optical Systems
XPS	X-ray Photoelectron Spectroscopy
XRF	X-ray Fluorescence
ZAF	Quantitative Algorithm









