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Chemical Science and Technology Laboratory
Technical Activities
1998

U.S. DEPARTMENT OF COMMERCE
Technology Administration
National Institute of Standards and Technology

Submitted to the Board on Assessment of NIST Programs,
National Research Council

Shown on the cover (clockwise starting at bottom):

A data screen from the NIST Mass Spectral Database, showing likely matches between the mass spectrum of an unknown compound with several compounds from the database -- this database contains over 130,000 fully-evaluated entries. This is one of many important data activities in CSTL that provides critical data resources needed by industry and the scientific community.

Atomic and molecular-scale mapping of surfaces is a new area of measurement science based on scanned probe methods that provide a means to probe interactions of surface-attached molecular species. This class of measurement methods holds great promise for surface chemical characterization with atomic-scale spatial resolution.

The characterization of Standard Reference Materials (SRMs) is a core activity of CSTL. The SRM shown is SRM 956, Electrolytes in Human Serum. For measurements in chemistry, chemical engineering, and biotechnology, the nation's traceability structure is based upon the availability of critically-evaluated measurement standards.

The development of critical biochemical measurements and methods advances the scientific basis and societal impact of biotechnology. The study and manipulation of the DNA molecule is one such focus in CSTL. Well-characterized materials have been produced that enhance quality assurance procedures of genetic testing (DNA Fingerprinting). Slab gel electrophoresis methods have been developed to detect single DNA-base mutations in the human p53 (anti-tumor) gene.

A micro-machined, thin-film gas sensor array (microhotplate) has three functional layers: a heater, a thermometer/heat distribution plate, and sensing film electrical contacts. These devices are being developed to provide inexpensive, real-time measurement technology with broad industrial applications, e.g., in process control, chemical identification, and automobile emissions measurements. The view across the image is about 500 micrometers.

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

U.S. DEPARTMENT OF COMMERCE, William M. Daley, Secretary
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Program Overview

Since its creation by Congress in 1901, NIST, then the National Bureau of Standards, has been the Nation's leading reference laboratory for measurements and standards with the express mission of supporting U.S. industry, commerce, scientific institutions, and all branches of the U.S. Government. The Chemical Science and Technology Laboratory (CSTL), one of the seven NIST Measurement and Standards Laboratories, is an integral part of the unique NIST mission to promote U.S. economic growth by working with industry to develop and apply technology, measurements, and standards.

Mission:

As the Nation's Reference Laboratory, the **mission of CSTL** is to provide the chemical measurement infrastructure to enhance U.S. industry's productivity and competitiveness, assure equity in trade, and improve public health, safety, and environmental quality. CSTL is a world class research laboratory recognized by the Nation as the primary resource for chemical, biomolecular, and chemical engineering measurements, data, models, and reference standards required to enhance U.S. industrial competitiveness in the world market. These capabilities are provided for the Nation - U.S. industry, government agencies, and the scientific community. CSTL seeks to accomplish its mission by setting and meeting the following goals:

- *Measurement Standards:* Establish CSTL as the pinnacle of the national traceability and international comparability structure for measurements in chemistry, chemical engineering and biotechnology, and provide the fundamental basis of the nation's measurement system.
- *Chemical and Process Information:* Assure that U.S. industry has access to accurate and reliable data and predictive models to determine the chemical and physical properties of materials and processes.
- *Measurement Science:* Address current and anticipate next-generation measurement needs of the nation by performing cutting-edge research in measurement science.

Organizational Structure:

CSTL is a multifaceted, synergistic organization with a broad customer base. The Laboratory has technical capabilities in analytical chemistry, surface chemistry and microanalysis, chemical and physical properties, process measurements and modeling, and biotechnology. The primary customers we serve are industry (chemical, electronics, automotive, petroleum refining, instrumentation, biotechnology, environmental technologies, and health care); federal, state, and local government agencies; standards and industrial trade organizations; and the academic and scientific community. CSTL is organized to reflect the technical expertise that is the foundation of our technical program and allows us to accomplish our mission. The Laboratory consists of five Divisions:

- Biotechnology Division,
- Process Measurements Division,
- Surface and Microanalysis Science Division,
- Physical and Chemical Properties Division, and
- Analytical Chemistry Division.

Each Division employs a group structure organized to achieve synergy and critical mass in its technical program areas. To accomplish its mission CSTL maintains expertise in a broad range of technical areas. Our technical staff consists of chemists, physicists, engineers, biologists, geologists, and computer specialists located at the major NIST sites in Gaithersburg, Maryland and Boulder, Colorado, as well as at the Center for Advanced Research in Biotechnology (CARB) in Rockville, Maryland and the Marine Environmental Health Research Laboratory (MEHRL) in Charleston, South Carolina.

To achieve its goals, CSTL maintains an experienced, well-educated professional staff. The permanent staff numbered 283 in FY98, in addition to 125 temporary and part-time employees. Also, there were almost an equivalent number (229) of guest researchers who work closely with CSTL staff. The technical capabilities of CSTL staff are extensive. CSTL technical staff (292) hold degrees in chemistry (172), physics (49), engineering (49), and in biology, geology, and computer science (22). A technical support staff of 33 augments the professional staff. Approximately 75 % of the technical staff hold PhD degrees.

The needs of our customers are reflected significantly in our program priorities. Customers purchase our products and services, e.g., SRMs, Standard Reference Data, and calibration services, collaborate with us through consortia and CRADAs, contract for our services, and interact through round robins, conferences, and workshops, and informally with our technical staff. Some of the CSTL outputs and interactions in FY98 are summarized in the following table. Our research program results in new measurement methods, critical information for design of new or improved chemical or biochemical processes, and analytical methods or procedures supporting new SRMs.

Div.	Pubs.	Talks	Committees[1]	Seminars	Conferences	CRADAs	Patents Issued	RMs/ SRMs	SRDs	Cals.[2]
830	7	27	41	10	3	0	0	0	0	0
831	112	135	59	43	8	6	1	4	1	0
836	71	103	105	11	7	10	0	6	1	649
837	112	107	87	10	11	3	0	12	2	2
838	190	104	122	59	3	7	0	4	10	4
839	126	133	124	33	7	5	0	221	1	344
Totals	618	609	538	166	39	31	1	247	15	999

[1] Committee totals include 63 editorships

[2] Calibrations were performed for over 340 customers

Division Key:

830	Laboratory Office
831	Biotechnology Division
836	Process Measurements Division
837	Surface and Microanalysis Science Division
838	Physical and Chemical Properties Division
839	Analytical Chemistry Division

Research Program Assessment and Evolution: We balance our programs among development of essential measurement standards and technologies and basic research to ensure a healthy science and infrastructural technology base for the future. Each Division in CSTL performs basic and applied research and maintains close contacts with the appropriate industrial and scientific communities to assess and anticipate the future measurement needs of our customer base. As part of our strategic planning process, in the fourth quarter of each fiscal year we assess and prioritize future needs and reorient our research program to reflect the changing needs of our customer base. In FY98 we began or strengthened five new program areas:

- Standards for Raman spectroscopy
- Chemical analysis at critical surfaces and interfaces
- Determination of non-metals in advanced materials,
- Computational chemistry, and
- Molecular scale materials characterization.

At the beginning of FY99 we began or enhanced five program areas:

- Measurement Methods and Standards for Next Generation Health Status Markers
- New Flow Traceability Paradigm
- Characterization of Ultra-Thin Films
- Kinetics/Thermodynamic Data for Industrial Processes
- Fluorescence Intensity Standards for Cell Cytometry

This is the fourth year that CSTL has re-oriented various aspects of its program to address anticipated demands from its customer base. Re-orienting parts of CSTL's research effort is accomplished with existing resources through identification of new areas where CSTL's work is anticipated to have significant impact on U.S. industry. Resources are redirected from activities where efforts have reached maturity and produced their anticipated results.

Major Facilities Additions: Major progress has been made with facility additions affecting CSTL operations in FY98. A state-of-the-art addition to the original facility at CARB (CARB IB) was completed in late FY97 and fully occupied this year, providing an additional ≈3,100 m^2 (28,000 ft^2) of modern laboratory space for biotechnology research. The three floors of the new building are staffed jointly by investigators from CSTL and the University of Maryland Biotechnology Institute and provide a significant expansion of this joint effort.

The Advanced Chemical Sciences Laboratory (ACSL) on the Gaithersburg Campus of NIST neared completion in FY98. The ACSL will provide CSTL with 7,605 m^2 (≈82,000 ft^2) of state-of-the-art laboratories. The ACSL building is scheduled for completion in mid-November of 1998. Following approximately three months of preparation, the Analytical Chemistry and Biotechnology Divisions will move into the ACSL in early 1999. We expect to complete the move of laboratories and in the late spring of 1999.

Technical Achievements:

Many noteworthy technical achievements were made by the CSTL scientific staff during FY98 that contributes to long term accomplishment of the CSTL goals. Examples of these are discussed briefly below. More detailed information about these activities can be found in the appropriate Division's technical reports.

Measurement Standards: International trade and industrial development are rapidly changing, becoming more global and highly competitive. During the decade of the 90's, global trade has become a central element in U.S. economic growth and is expected to remain so well into the next millennium. The substantial dismantling of tariff-based trade barriers during this decade has resulted in increased levels of world trade. However, U.S. exports significantly lag those of our trading partners. Although tariffs are no longer trade barriers, many technical barriers to international trade remain that effectively control access to markets. Local and regional product conformity testing requirements contribute significantly to exclusion of U.S. exports from foreign markets.

Recognition of measurements and standards among nations is the responsibility of National Metrology Institutions (NMIs) such as NIST. Measurement and standards issues have become key elements in trade issues because they are intimately associated with product conformity testing that can be misused as a technical trade barrier. In this arena, recognition of the equivalence of measurement standards can be critical to recognition of the conformity of U.S. products in global markets.

For many years CSTL has participated and lead NIST efforts to compare measurement standards as part of U.S. obligations of the Treaty of the Meter. The International Committee on Weights and Measures (CIPM), established under the Treaty of the Meter, is charged with developing international comparisons of primary measurement standards. The increased prominence of measurements and standards issues in international trade has placed additional emphasis on comparison activities, significantly broadening the scope of such efforts.

Recently, several regional metrology organizations (RMOs) have come into existence, propelled by the increased importance of trade among nations within various regions. These organizations include SIM (Systema Interamericano Metrologia – comprising North and South America), NORAMET (the North American Metrology Cooperation), APMC (the Asian-Pacific Metrology Cooperation), and EUROMET (the Metrology Organization of the European Union). Planning activities and working relationships have been established among regional metrology organizations and the CIPM to develop a global system of recognition of measurements and standards. CSTL has been very active in these efforts, and comparison efforts for both chemical and physical measurement standards have been pursued aggressively primarily by the two CSTL Divisions having major responsibilities in this arena, the Analytical Chemistry and Process Measurement Divisions.

Benchmarking of CSTL Measurement Capabilities: CSTL is responsible for development and dissemination of the SI Base Units of temperature and the amount of substance (mole) and for the derived units of pressure and vacuum, humidity, fluid flowrate, liquid volume and density, and airspeed. We have made an initial assessment of standards comparability based on our long involvement in the comparison of measurement standards with other NMIs. Many of these efforts have been and are conducted under the auspices of the Consultative Committees of the CIPM, in addition to many bi- or multi-lateral collaborative activities. Our initial assessment of CSTL's capabilities is given in the following tables using three broad comparability classes that are defined as follows:

• Best in Class	The only NMI known to be at this level of practice;
• State-of-the-Art	Other NMIs at this level of practice; and
• Not State-of-the-Art	Below the level of practice by other NMIs.

SI Base Units

Quantity (Unit)	Dissemination Range	Relative to Other NMIs
Temperature (K)	0.65 K – 25 K	Best in Class
	13.8 K – 273.16 K	Best in Class
	83.8 K – 934 K	Best in Class
	273.16 K –1235 K	Best in Class
Amount of Substance (mol)		
Inorganics	(10^{-6} – 10^{-1}) mol/mol	Best in Class
Organics	(10^{-6} – 10^{-1}) mol/mol	Best in Class
Gases	(10^{-15} – 10^{-1}) mol/mol	Best in Class
Complex Matrices	(10^{-10}– 10^{-1}) mol/kg	Best in Class
Pure Chemicals	$\approx 10^{0}$ mol/mol	State-of-the-art
pH	13 – 1	Best in Class

As part of its responsibility for the SI Base Unit of temperature, CSTL has put forth significant effort to realize and disseminate the temperature unit over the full contact range of the International Temperature Scale of 1990 (ITS-90). NIST is the first NMI to have achieved this capability. As yet no other NMI has realized the new scale over its full range. Comparison of temperature standards has been an activity of long standing among those NMIs with the requisite capabilities. Recently greater emphasis has been placed on this activity. CSTL's efforts in this area are described in several parts of this report.

From the perspective of SI unit classification, all chemical measurement standards are measures of the amount of substance, the mole. However, the breadth of technologies and expertise necessary to develop and disseminate chemical measurement standards effectively considerably exceeds that generally necessary for a single physical measurement unit. Six general chemical measurement areas are normally identified where NIST and its counterpart NMIs develop and disseminate measurement standards and have comparable capabilities. However, within each area there may be several subcategories that have unique procedures and materials necessary to effect a comparison of standards. Comparison efforts in the chemical measurement standards area began more recently than comparison of physical standards. Comparisons of the seven derived measurement units (six physical and one chemical), for which CSTL is responsible, have varying degrees of activity associated with them. Discussion of the efforts supporting these activities are given later in this report in the sections for the Process Measurements and Analytical Chemistry Divisions.

Derived Units

Quantity (Unit)	Dissemination Range	Relative to Other NMIs
Pressure and Vacuum (kg, m, s)	Vacuum < 1 Pa	State-of-the-Art
	0.1 Pa – 350 kPa	Best in Class
	10 kPa – 270 MPa	State-of-the-Art
Liquid Density (kg, m)	(0.85 – 1.1) g/cm^3	State-of-the-Art
	(0.65 – 3.0) g/cm^3	State-of-the-Art
Liquid Volume	(5 – 7600) L	State-of-the-Art
Humidity (Moisture Concentration In Gases) (mol)	5 nmol/mol – 10 mmol/mol	Best in Class
	1 µmol/mol – 0.1 mol/mol	Best in Class
Liquid Flowrate (kg, s)	0.1 g/s – 2 x 10^4 g/s (Hydrocarbons)	Best in Class
	0.01 kg/s – 600 kg/s (Water)	State-of-the-Art
Gas Flowrate and Leak (m, s)	(10^{-14} – 10^{-6}) mol/min	Best in Class
	(0.01 – 1000) cm^3/min	State-of-the-Art
	(0.001 – 78) m^3/min	Not State-of-the-Art
Air Speed (m, s)	(0.15 – 10) m/s	Best in Class
	(4.0 – 67) m/s	Best in Class
Conductivity (A, m)	(5 – 10^{-5}) µS/cm	Best in Class

International Comparison Database: NMIs and the BIPM are developing a framework for establishing mutual recognition of measurements and national measurement standards. Such recognition will be based on measurement and calibration capabilities that are supported by measurement comparison data. To limit the burgeoning number of bilateral and multi-lateral comparisons that must be conducted, the NMIs and Consultative Committees of the International Committee on Weights and Measures (CIPM) are in the process of identifying key comparisons. These will be strategically designed to leverage the widest possible range of measurand levels and types. A significant body of comparison data already exists in the pertinent literature. However, there has been no systematic effort to catalogue or organize it so that we can effectively answer how such measurement data address a particular specification or trade requirement. NIST leads the world in the development of a database for international comparisons. CSTL leads the NIST effort, directing a team comprising staff from several NIST organizational units.

The approach we have taken is to develop a relational database that:

- contains all the necessary details of comparisons and participants,
- contains data as actually reported and published, and
- is limited to comparisons of previously established quality.

Data entry and database administrations are implemented using a personal computer platform and commercially available database software. Users access the database via the WEB. The interface allows flexible search, querying, and data presentation options. Results of comparisons are retrieved based on the user's search criteria. Differences between sets of results from any two participants or any participant and the comparison reference value are presented. These differences and their uncertainties are combined to allow evaluation of measurement and national standards comparability.

The BIPM and other NMIs are now collaborating with NIST to ensure that all types of metrology areas and comparison designs can be accommodated. CSTL will also lead the NIST effort to implement the database within the SIM. Comparison data from the SIM and the other RMOs will be entered into the database to link regional comparison data with the CIPM efforts. Furthermore, NIST will begin to implement the database to organize calibration data within the U.S. system of measurement traceability. The ultimate goal is to provide a recognized and readily available means to compare measurement data anywhere along the chain of national systems of traceability and international comparability.

Measurement Standards Infrastructure: CSTL establishes and maintains the infrastructure that provides national traceability and assesses and realizes international comparability for chemical and certain physical measurements. Vertical traceability of chemical and physical measurements in the U.S. is supported and strengthened by developing improved primary measurement standards and methods. The provision of instrument calibration and test services is a primary means to disseminate U.S. national standards for physical quantities to industrial users and federal and state government laboratories. Similarly, the development of SRMs is the primary method for dissemination of the chemical measurement standards. During FY98 CSTL provided 66 % of the SRM units sold through the NIST Standard Reference Material Program and 5 % of the calibration services provided through NIST's Office of Measurement Services.

Chemical Measurements: Although considerable emphasis has been placed on the assessment of the comparability of chemical measurement standards in the international arena for several years, CSTL continues to lead NIST in its efforts to define, establish, and broaden the national infrastructure for chemical measurements. Currently, NIST provides nearly 1300 different types of SRMs and in FY98 sold nearly 37,000 SRM units to approximately 6,650 unique customers; approximately 21,000 units of these represent about 850 different types that are certified for chemical composition. Not only do these efforts broaden the U.S. chemical measurement infrastructure, providing traceability of chemical measurements, but they are also the foundation of CSTL's activities in the comparison of standards in the international arena.

The provision of chemical measurement standards and technologies also involves partnerships with other federal agencies, state governments, and private sector institutions. CSTL's goal in these interactions is to ensure the integrity of chemical measurements made in a variety of applications. Measurement systems supporting the environment are undertaken collaboratively with the Environmental Protection Agency (EPA) and the National Oceanic and Atmospheric Administration (NOAA) in a number of areas:

- Proficiency testing studies to assess the competence of public and private laboratories making analyses required by the Clean Water and Safe Drinking Water Acts.
- Provision of quality assurance of measurement protocols for laboratories making measurements of organic contamination in marine sediments and tissues.
- Development of primary standards for ambient levels of methane (CH_4), nitrous oxide (N_2O), dichlorodifluoromethane (CFC-12), and trichlorofluoromethane (CFC-11) to support measurement of these species by the atmospheric research community.
- Development of gas standards supporting engine exhaust measurement at levels required for the next generation of automobiles.
- Completed activities involving measurements of heavy metals, pesticides, and polycyclic aromatic

hydrocarbons (PAHs) in soil, water, food, and indoor and outdoor air as part of the National Human Exposure Assessment Study.

Chemical measurement and standards needs related to healthcare continues to be a significant CSTL program. FY98 marks a change in our 15-year association with the National Cancer Institute (NCI) to provide measurements and standards necessary to study the effects of micronutrients on high-risk human populations. At the request of the participating laboratories, CSTL will continue its efforts at a reduced level after NCI involvement ends. Related efforts also support the forensic testing community and the food industry.

Comparison of chemical measurement standards continues to be a growing area of effort for CSTL. For the past five years, NIST has worked with the **Netherlands Measurement Institute** (NMi) to establish equivalence in gas standards between the U.S. and Europe. The present equivalence agreement demonstrates comparability within ± 0.5 %. As a result of this agreement EPA now recognizes the Equivalence Agreement in its regulations so that both U.S. and European specialty gas producers can use NMi standards when preparing EPA protocol gas standards.

CSTL continues to expand it involvement in the comparison of chemical measurement standards with NMIs of other nations. These efforts continue to expand both through existing arrangements and in response to increased requests for NIST participation. In many of these areas, NIST is the preeminent NMI. Comparison activities that have been operating with various NMIs in specific chemical measurement areas include:

- the **Danish Institute of Fundamental Measures** (DFM) and the **Hungarian Office of Measures**, (OHM) for standards for electrolyte conductivity,
- the **Physikalisch-Technische Bundesanstalt** (PTB, Germany) for pH measurement standards,
- with the National Institute of Materials and Chemical Research (NIMC, Japan) and the Bundesanstalt fur Materialforschung und -prufung (BAM, Germany) for elemental solution standards, and
- **NIMC** for volatile organic compound standards.

Chemical measurement efforts continue to expand within SIM and NORAMET. CSTL was involved in a number of planning efforts aimed at developing comparison of various chemical measurement standards in FY98. Training opportunities for metrologists from SIM member countries will be provided by CSTL in FY99 as a prelude to formal comparison efforts.

CSTL establishes and maintains the chemical measurement infrastructure for national traceability and for assessing international comparability. The provision of SRMs and NIST Traceable Reference Materials (NTRMs) are important tools in this effort. These capabilities are used to establish and maintain chemical measurements within the U.S. and to compare NIST primary methods and standards with other national metrology laboratories for chemical measurements. SRMs are certified reference materials issued under NIST trademark that are well-characterized using state-of-the-art measurement methods and/or technologies for chemical composition and/or physical properties. Because CSTL does not have all of the resources necessary to provide the quantities and specific varieties of SRMs needed to meet the increasing needs of U.S. industry, the NTRM program has been established. An NTRM is a commercially produced reference material with a traceability linkage to NIST standards for chemical measurements. CSTL establishes the criteria and protocols necessary to maintain the traceability linkage, which are tailored to meet the needs of the metrological community to be served. Ten specialty gas manufacturers have worked with NIST to certify nearly 5,600 NTRM cylinders of gas mixtures. These, in turn, have been used to produce approximately 400,000 NIST-traceable gas standards for end-users. The NTRM program has significantly improved the quality of these standards and has been critical in supporting a variety of uses including the implementation of Title IV (SO_2 emissions trading) of the 1990 Clean Air Act. The NTRM program has been a great success, and it has expanded to include other mature, high volume measurement areas such as optical filter standards for spectrophotometers used in chemical concentration measurements, spectrometric solutions, and metal alloy standards.

Physical Measurements: In FY98 the Process Measurements Division achieved an important NIST goal in completing the realization of ITS-90 in terms of its fundamental definition. Having completed the NIST realization of the scale, current activities focus on comparisons with other NMIs and examination of the internal consistency (uniqueness) of the scale. Comparisons of standards are being carried out in two arenas. The first, under the auspices of the Consultative Committee on Thermometry (CCT) of the CIPM, involves four key-comparisons in the region 0.65 K - 1235 K. CSTL participates in all, coordinates one, is regional sub-coordinator for another, and has supplied the fixed-point cells and reference thermometers for another key comparison. Planning activities with other SIM members are anticipated to result in some key comparisons within SIM in coming years. Joint efforts continue with the Physics Laboratory to improve the accuracy of thermodynamic temperature measurements and standards in the range above 500 K.

CSTL provides national standards and calibration services over 16 decades of pressure, from 10^{-7} Pa to 10^{9} Pa. The need to engage in international comparisons has grown in importance with CSTL participating in six key comparisons of pressure and vacuum standards organized under the Consultative Committee for Mass and Related Quantities of the CIPM. We lead three of these efforts by serving as pilot laboratory. For sub-atmospheric and vacuum comparisons CSTL has developed new transfer standards, instrumentation, and protocols. Within the five SIM regions, multi-laboratory comparisons for near-atmospheric pressure measurements have involved a multi-day training program at NIST and visits by NIST staff to each participating laboratory. In some cases, this effort involves equipping the participant with reference standards and peripheral equipment.

In measurement of fluid flow rate, CSTL provides gas flow and leak-rate standards and calibrations over the range from 10^{-14} mol/s to 10^{2} mol/s and similar services for liquid flows in the range from 10^{-3} L/s to 10^{3} L/s. Research efforts are directed at developing both advanced transfer standards and primary standards. Activities include:

- Development of ultra-stable, laminar flow transfer standards in the range 10^{-7} mol/s to 10^{-3} mol/s with demonstrated stability over the course of three years of ±0.1 %.
- A program to reduce the uncertainty of our primary gas flow standard in the range 10^{-3} mol/s to 10^{-1} mol/s to 0.05 % or less (k=2) and to use modern control and instrumentation to achieve higher accuracy, lower cost, and reduced turn-around time for these calibration services;
- Extension of the range of the range of gas flow conditions over which NIST provides traceable calibrations by annexation of facilities at U.S. secondary calibration laboratories. The Internet will be used to provide access for metrological control and to an in-line, ultrasonic travel-time flowmeter which will provide information on the flow environment as well as serving as a check standard.
- Developing new metering technology and calibration facilities to address flow measurement needs in reactive or corrosive gases.

CSTL, working with the **National Fluid Power Association,** developed SRM 2806 Medium Test Dust In Hydraulic Fluid, that serves as the principal reference material for contamination control in the fluid power industry. SRM 2806 replaces a test material that had been accepted and used internationally by the industry for over 25 years. SRM 2806, and its companion reference materials, RM 8631 and RM 8632, are required in the national standard method NFPA/T2.9.1 R2 and the international method ISO/FDIS 11171, and impacts numerous ISO documents related to fluid power. SRM 2806 significantly advances the accuracy and precision of contamination monitoring and liquid particle filter testing.

CSTL continues to work closely with the **Department of Justice** to provide human identity testing standards. Laboratory testing for the new SRM 2392 Human Mitochondrial DNA, was completed in FY97. Validation and sequencing studies were completed this year with production of the SRM scheduled for FY99.

Chemical and Process Information: Realistic design and modeling of chemical processing systems is critically dependent upon chemical, physical and engineering data to accurately describe materials properties and processes and to model the mechanisms controlling these systems. CSTL activities provide or contribute to:

- standard/evaluated benchmark data for properties of important substances, classes of substances and systems,
- data collections, data prediction methods, and models to meet high priority/immediate industrial and/or national needs,
- development of consensus standards for key properties, substances, and processes, and

- protocols or procedures for data access, facilitation of data exchange, and dissemination of appropriately formatted data.

CSTL is the source of most (69 %) of the databases provided by the NIST Standard Reference Data Program. The majority of this activity is found in the Physical and Chemical Properties Division. Dissemination of data via the Internet is the next step in the evolution of reference data availability, beginning with printed reference books, proceeding through various forms of electronic media, i.e., magnetic discs to CD-ROMs, to web-accessible dissemination. A major effort for CSTL was the development of the **NIST WebBook (http://WebBook.nist.gov)** which provides ready access to chemical reference data. The WebBook provides Internet access to an extensive set of chemical data with a common interface featuring ease of use and ready expansion capability. The major thrust of the WebBook is to supply data from NIST evaluations of chemical and physical property data. The expanding role of the WebBook is to provide a resource for chemical data from all sources. Between 5000 and 8000 users per week use the Chemistry WebBook. It is becoming a well-recognized resource for professionals and students. The fraction of returning users in a given week is 45 % to 55 %, an indication of its use as a reference information tool.

During FY98 the fourth edition of the WebBook was released, increasing its content from ≈ 22,300 compounds to more than 31,600 compounds. Vibrational and electronic data on ions and radicals and spectroscopic constants for diatomic molecules were added. The fifth release, planned for FY99, will incorporate corrected and updated vapor pressure data, Henry's law data, and critical constant data, with significant increases to many of the thermodynamic data types already present.

A new effort in **Bioinformatics** was initiated in FY98. Bioinformatics develops and applies computational methods to large biomolecular structure and sequence databases to identify, analyze, or predict the structure and/or function of new biomolecular species. These expanded capabilities will enhance CSTL's research programs and aid industry in the efficient use of chemical and biochemical data in the development of new products and processes. A major effort this year involved a collaboration with Rutgers University, the University of California San Diego Supercomputer Center, and the CSTL Biotechnology Division to establish the **Research Collaboratory for Structural Bioinformatics** (RCSB). This organization provides a unique framework for web-based resource developments of general interest to the academic, private, and industrial research communities. The strength of the organization is illustrated by the successful bid for the NSF/DOE/NIH funded **Protein Data Bank**. The RCSB (http://www.rcsb.nist.gov/) will assume the responsibilities of managing and distributing the Protein Data Bank during FY99.

CSTL continues to provide industry with **high-accuracy, physical property data for alternative refrigerants**, CFC and HCFC refrigerant replacements that do not deplete stratospheric ozone. These data are provided in the REFPROP database, which was completely revised for its FY98 release. This database calculates the thermodynamic and transport properties for a wide variety of fluids and fluid mixtures being investigated for use in refrigeration equipment. Research in this area is shifting to mixtures and their transport properties. Additionally, the modification to the extended corresponding states (ECS) model of these systems, developed previously by CSTL, was shown to be a significant improvement over earlier models. The ECS model was adopted by Annex 18 of the International Energy Agency.

Mass spectrometry continues to be the most widely used measurement tool employed by the industrial and research communities to identify unknown chemicals. For the industrial community mass spectrometry is also an important process monitoring and quality control tool. Like many other analytical techniques, it is best used with a library of reference spectra. Mass reference spectra provided by CSTL have become an integral part of these systems; U.S. mass spectrometer manufacturers routinely include the NIST reference database with their instruments. CSTL has substantially improved the quality of this database over the last several years. The new release of the NIST mass spectral database – **NIST 98** – provides a fully evaluated database of mass spectra for 107,886 compounds. Structures are provided for 107,829 compounds and replicate spectra for 13,205 compounds. Because each spectrum has been individually evaluated, NIST 98 represents the best collection of mass spectral data ever assembled. Additionally, advances in the algorithms needed for searching the database have been developed and extensively tested, both for their inherent functionality and to compare them to other search algorithms. These have proven to be significant improvements in search capabilities. 3,864 copies of the mass spectral database were sold during FY98.

CSTL has developed and released a spectral reference database for open-path FT-IR measurements of chemical emissions and hazardous air pollutant molecules. Reference spectra for 21 hazardous air pollutants on the EPA's priority list were developed from primary standard gas mixtures prepared using starting materials of assessed purity and procedures to minimize contamination. The final concentrations of these standards were verified by gas chromatography using several independently prepared calibration mixtures. **NIST Standard Reference Database (SRD) 79, version 1.00** is available on a CD-ROM or from the Internet. A digital signature accompanies each data file to ensure its integrity and traceability to NIST. In future years, additional quantitative spectra will be added to the database for the compounds listed in the Clean Air Act Amendment of 1990 as well as additional compounds that contribute to global warming and ozone depletion.

Measurement Science: CSTL maintains a strong research program to support the Nation's measurements and standards infrastructure, establish new measurements capabilities supporting new or advanced technology development and dissemination, and provide a fundamental basis for global scientific decision making. There have been many noteworthy research achievements by CSTL scientists and engineers during FY98. A Brief discussion is presented below. More detailed information is contained in the technical reports of the respective Divisions found in the remainder of this report.

The Surface and Microanalysis Science Division is investigating methods to improve the sensitivity, stability, and specificity of **molecular secondary ion mass spectrometry (SIMS)** through the use of polyatomic primary projectiles as sputtering sources. A SF_5^+ polyatomic beam has been developed as a means to improve characterization of biological materials. The secondary ion signals obtained by *integrating* over the depth of a 220 nm glutamate film using SF_5^+ were enhanced by as much as a factor of 700 relative to Ar^+ bombardment. This work is the first demonstration of depth profiling through an organic film while maintaining characteristic molecular secondary ion signals. This technique is also being investigated for improved sensitivity in materials used in semiconductor manufacturing.

The Process Measurements Division is developing new optical methods for **species specific, partial-pressure measurements and standards.** These are important for monitoring process gases in both vacuum and at higher process pressures. By combining previously developed theoretical models, a new and unique light source, and specially designed ring-down cavities, CSTL is the first to demonstrate high sensitivity levels achievable using single-mode cavity ring-down spectroscopy (CRDS) with pulsed lasers. Ring-down signals can be measured with a standard deviation of 0.02 – 0.05 %, a factor of 4 to 10 larger than the ultimate levels achievable (the shot-noise limit). Absorption sensitivity of $\sim 10^{-10}$ cm^{-1} with a 10-cm cavity has been achieved, a 20-fold improvement in sensitivity for this unique approach compared with prior CRDS measurements. Based on these results, a pressure measurement or integrated line-strength measurement imprecision of < 0.3 % has been demonstrated providing a pathway for CRDS measurements to have an imprecision competitive with prevailing **primary standards in the vacuum and low-pressure range** (10^{-5} Pa to 10 Pa). Application of these methods to water **partial pressure measurements** is anticipated to yield ultimate sensitivities below 10^{-6} Pa for vacuum measurements or equivalently 100 picomol/mol for measurements of moisture in gases, e.g. humidity.

Improved measurement and modeling techniques are needed to characterize enzymatic transformations critical to **industrial applications of biocatalysis and metabolic engineering**. Discovery of promising new metabolic pathways that hold promise for commercial scale chemical manufacturing from renewable resources, e.g., glucose from crop spoilage, is occurring at an increasing rate and is expected to have a significant economic impact on the U.S. chemical industry. CSTL is investigating two systems as models for metabolic engineering. For the biosynthetic pathway leading from **glucose to chorismate and its aromatic derivatives**, a database combining existing structural and other information with new measurements from the biothermodynamics laboratory has been created. Cytochrome P450 and its electron transfer partners putidaredoxin (Pdx) and Pdx reductase are also being investigated because they stereospecifically hydroxylate a variety of carbon rich compounds. They are of interest to both the chemical synthesis and bio-remediation industries.

The newly commissioned high-field NMR facilities at CARB have expanded the research activities of the structural biology group. The state-of-the-art facility provides the infrastructure for developing new methods for enhancing the sensitivity and resolution of **heteronuclear, multiple resonance experiments** applied to isotopically-enriched nucleic acids. These methods are of key importance to industrially crucial screening processes for therapeutic compounds that disrupt clinically important nucleic acid-protein interactions

Recent research efforts in **organic mass spectrometry** focused on electro-spray ionization as a tool for quantitative determination of proteins in biological matrices. Reference methods for important biomarkers such as troponin-I (a new marker of myocardial infarction), glycohemoglobin (an important new marker for diabetes), serum thyroxine (an important marker for thyroid function), and cortisol (a marker for endocrine function) are being established.

Measurement of chemical reactions is a challenging area of research. CSTL has several activities focused on probing the chemical state of surfaces. Research efforts in the Physical and Chemical Properties Division have extended cavity ring-down spectroscopy (CRDS) to evanescent wave CRDS for the study of chemical reactions at surfaces. EW-CRDS employs a miniature, monolithic, total-internal-reflection (TIR) ring cavity of regular polygonal geometry with at least one convex facet for stability. Evanescent waves generated by TIR probe absorption by matter very near the external surface of the cavity. The broadband nature of TIR circumvents the narrow bandwidth restriction imposed by dielectric mirrors in conventional gas-phase cavity ring-down spectroscopy. The advantages of cavity ring-down and ATR spectroscopies allow EW-CRDS to achieve a synergistic new technology that exceeds existing optical absorption techniques in sensitivity by many orders of magnitude and may ultimately achieve single molecule detection. Experimental results have demonstrated a detection limit of <100 parts-per-million of a monolayer adsorbed at the surface of the TIR cavity.

Another collaborative research effort between staff in the Surface and Microanalysis Science Division and Physics Laboratory staff is focused on a simple, robust approach to the acquisition of vibrationally resonant sum-frequency generation (SFG) spectra, for the *in-situ* study of chemistry at interfaces. Although vibrationally resonant SFG is a powerful probe of buried interfaces, such as the solid-liquid or liquid-liquid interface, where standard, linear, infrared absorption-spectroscopy is usually impossible, it has proven to be difficult to implement, because it traditionally involves tuning a custom-built, narrow-bandwidth IR laser through the molecular resonances of interest. A commercial, ultrafast, amplified Ti-sapphire pumped optical parametric amplifier generates broad-bandwidth IR pulses tunable from 2.5 μm to 12 μm. By mixing these IR pulses with narrow-bandwidth 800 nm pulses derived from the amplified Ti-sapphire pump, SFG is generated at the interface. The resultant sum frequency light is dispersed by a spectrograph and detected with a high-resolution CCD camera over a 500 cm^{-1} spectral region without tuning the IR source. Relative to SFG spectra reported in the literature acquired with traditional techniques, the spectra taken with our new method are of superior quality and require much less data acquisition times.

Conferences and Workshops:

CSTL sponsored or co-sponsored conferences and workshops that span the range of its activities. CSTL was a co-organizer of the **11th Annual Workshop on Secondary Ion Mass Spectrometry** in Austin, TX on May 11, 1998. This conference brought together over 130 international researchers from the field of surface analysis.

CSTL led a multi-agency-sponsored **International Workshop on Green Chemistry and Engineering: Global Collaborations**. This workshop was held in Washington DC on July 2, 1998, in conjunction with the 2nd Annual Green Chemistry and Engineering Conference. A panel of science, technology and public policy experts from Asia, the Americas, and Europe were assembled to discuss industrial and public policy perspectives that drive scientific research and engineering of sustainable chemical processes in their region or nation, and to propose productive and creative solutions to mutual environmental concerns.

Two NATO Advanced Study Institutes - **Energetics of Stable Molecules and Reactive Intermediates** held in Castelo Branco, Portugal and **DNA Damage and Repair; Oxygen Radical Effects, Cellular Protection and Biological Consequences** held in Tekirova-Antalya, Turkey were organized by CSTL staff.

Annex 18 of the International Energy Agency, an activity initiated and led by CSTL since 1990, held its final meeting in Trondheim, Norway on June 8, 1998. In the last of a series of equation of state comparisons, the high-accuracy equation developed at NIST for the hydrofluorocarbon refrigerant R143a was declared the international standard for this fluid.

The opening of the new CARB IB laboratories was celebrated at a symposium held on April 3-4, 1998, in conjunction with CARB hosting the annual meeting of the **International Network of Protein Engineering Centers** (INPEC) on April 4-7. Over 200 scientists from academic, government, and industrial laboratories attended the symposium, which focused on forefront issues in structural biotechnology.

A workshop on **Standards for Nucleic Acid Diagnostic Applications**, was held at NIST, March 15-18, 1998, to determine what standards for nucleic acid diagnostics were needed by the emerging molecular diagnostics community.

CSTL and the National Voluntary Laboratory Accreditation Program held a workshop, **NIST Accreditation Program for Providers of Proficiency Testing**, in Arlington, Virginia on January 16, 1998. Representatives of laboratories testing drinking water and wastewater for regulated chemical, microbial, and radiochemical, parameters attended.

Awards and Recognition:

Many CSTL scientists and engineers received awards and recognition in FY98. Achievements by the Surface and Microanalysis and Analytical Divisions were recognized with a **Certificate of Excellence from the Department of Defense** for the five year period 1992-1997 "In recognition of your exemplary contributions as a member of the Air Force Technical Applications Center Materials Product Team ... leading to award of the National Defense Meritorious Unit Citation ... team distinguished themselves by providing exceptional support to ... the United States Air Force and Policy makers up to and including the President of the United States."

Kevin Ridge was awarded **the Karl Kirchgessner Foundation Prize** for his pioneering work on the folding and assembly of integral membrane photoreceptor rhodopsin, a model system for drug receptors of immense biomedical importance.

Lee J. Richter received the **Maryland Distinguished Young Scientist Award** in recognition of his detailed studies of photo-induced surface chemistry.

Steve Semancik was elected a **Fellow of the American Vacuum Society** for his outstanding contributions to the understanding of the chemical and electronic properties of oxides and catalytic metals.

Robert R. Greenberg was elected a **Fellow of the American Nuclear Society** in recognition of his contribution to the development of high-accuracy/high-precision nuclear analytical methods and quality assurance procedures, and the application of these methods to the certification of Standard Reference Materials.

Gary Kramer received the **Association for Laboratory Automation Achievement Award** for scientific contributions and continuing efforts in the field of laboratory automation. Thorsten Richter and Chris Piotrowski won the 1st and 2nd poster presentation prizes at the 98 Meeting of the 1998 ALA annual meeting.

Robert E. Huie and Wing Tsang received the **Research and Development Achievement Award of the Army Research Laboratory** for work on halon replacements for ground fighting vehicles.

George Mattingly received the **Lewis M. Moody award from the American Society of Mechanical Engineers** for his paper "Flow Measurement Proficiency Testing for International Comparison and Traceability". This award is given for the paper of "most practical value to mechanical engineering" presented at the Annual Meeting of the ASME.

W. Robert Kelly received a **1998 Federal Laboratory Consortium Excellence in Technology Transfer Award** for development and transfer to the aerospace industry an analytical technique for advanced casting processes. This award was shared with several staff members of the NIST Materials Science and Engineering Laboratory.

George Lamaze received the **ASTM Award of Appreciation** given by Committee E-10 on Nuclear Technology and Applications in appreciation of his many years of outstanding and dedicated service to Committee E-10 and its subcommittees.

Two CSTL staff members were awarded the **Department of Commerce Silver Medal:**

- Barbara Levin was recognized for excellence in her guidance and management of committee activities that deal with research involving human subjects at NIST and at the Department of Commerce.
- Gary Mallard was recognized for developing the NIST Chemistry WebBook, the world's most comprehensive collection of chemical reference data available on the Internet.

Five 1998 **Department of Commerce Bronze Medals** were awarded to five CSTL staff members.

- Robert F. Berg was recognized for measuring the viscosity of xenon near its critical point with unprecedented accuracy onboard the Space Shuttle.
- Kenneth D. Cole was recognized for development of preparative-scale separation technologies for different physical forms of DNA, the first use of electrochromatography for the isolation of large, fragile DNA molecules.
- John F. Houser was recognized for outstanding contributions to the development of primary standards for liquid volume and density measurements, for provision of calibration services of the highest quality, and for exceptional support to customers.
- Robert A. Fletcher was recognized for leadership in all aspects of the development and issuance of reference materials for calibrating particle contamination monitoring devices.
- W. Robert Kelly was recognized for development and application of isotope dilution mass spectrometry methods to chemical measurements and standards problems of industrial relevance.

Stephen E. Stein and Gary Mallard received T**he Slichter Award** for building close ties between the manufacturers and users of mass spectrometers and NIST. The Slichter Award is given by NIST in recognition of achievements by NIST staff in building or strengthening ties between NIST and industry.

Several CSTL staff members received the **NIST Measurement Services Award**. Peter J. Linstrom was recognized in the reference data category for designing the structure of the NIST Chemistry WebBook. Archie Miiller and Charles R. Tilford were recognized in the calibration category for their outstanding efforts in extending the range of NIST's primary calibrations of vacuum by an order of magnitude via high-accuracy manometry. Pamela M. Chu and Franklin R. Guenther were recognized in the reference data category for the development of the Quantitative Infrared Database to support remoted sensing of hazardous air pollutant molecules.

The NIST Chapter of Sigma Xi recognized Karl K. Irikura with its **Outstanding Young Scientist Award** for research on computational thermochemistry and Rastislav Levicky for **the best postdoctoral poster at this year's Sigma Xi Post Doctoral Poster Presentation**. His work was titled: "Using Self-Assembly to Control the Structure of Surface-Tethered DNA".

The **CSTL Technical Achievement Award** was awarded to two groups in FY98. Robert A. Fletcher, Jennifer R. Verkouteren, Eric S. Windsor, John A. Small, Eric. B. Steel, David S. Bright, Walter S. Liggett (ITL) and Robert J. Gettings (TS) were recognized for development and issuance of SRM 2806 Medium Test Dust in Hydraulic Fluid and two associated Reference Materials, RM 8631 and RM 8632. Andrew C. Pipino, Jeffrey W. Hudgens, and Robert E. Huie were recognized for developing evanescent-wave cavity-ring-down spectroscopy as a new tool for studying chemical reactions at interfaces.

Technical Highlights:
In the following pages, recent activities, technical directions, and accomplishments of the CSTL Divisions are presented. Division overviews

provide a general review of the activities of each Division and are followed by articles describing achievements in specific technical areas.

II. Biotechnology Division (831)

Gary L. Gilliland, Chief

A. Division Overview

Mission:
The Biotechnology Division is the focus of the NIST effort addressing critical measurement and data needs for the rapidly developing biotechnology industry. The mission of the Biotechnology Division is to provide measurement infrastructure necessary to advance the commercialization of biotechnology. This is achieved by developing a scientific and engineering technical base along with reliable measurement techniques and data to enable U.S. industry to produce biochemical products quickly and economically with appropriate quality control. The Division has established a variety of long-range research programs to maintain critical expertise needed for the development of advanced measurement methods, Standard Reference Materials and databases for use by industry and other research enterprises. It fosters collaboration among NIST scientists conducting biotechnology research, and raises the visibility of the NIST Biotechnology program, which leads to enhanced collaborations with industry, universities and other government agencies.

Programs:
To plan and guide Division research programs effectively, Division scientists are active in many forums that provide feedback on the long-term and short-term scientific and technological needs for biotechnology commercialization. These activities supplement the high level of Division participation in scientific meetings and topical workshops. For example, during FY98 the Division continued active participation in the Biotechnology Industry Organization (BIO), in the IUPAC Commission on Biophysical Chemistry, and in the ASTM Committee E-48 on Biotechnology. Division members were also active participants in a number of important workshops held at NIST. The Division also worked closely with the NIST Advanced Technology Program (ATP) in a variety of ways. Division members served as NIST technical representatives in the annual review of a number of active ATP grants. They also presenting the results of Division research programs in ATP-sponsored workshops and public meetings. Additionally, it should also be noted that Division members have been involved in fundamental research that is directly related to ATP focus areas, and also involved in research directly related to specific ATP projects. Throughout the year, the Biotechnology Division continued to play a major role in the planning and coordination of Federal biotechnology research through memberships in the working groups associated with the Subcommittee on Biotechnology of the National Science and Technology Council (NSTC). Involvement in these activities assures that the Biotechnology Division is an active participant in the decision making process for prioritizing and directing funding of federal research especially in areas that impact the private sector.

The staff of the Biotechnology Division consists of 59 NIST employees and a comparable number of contract researchers, guest scientists, and postdoctoral fellows. The Division is organized into four groups: (1) **DNA Technologies**; (2) **Bioprocess Engineering**; (3) **Structural Biology**; and (4) **Biomolecular Materials**. In addition, in FY98 a significant effort in **Bioinformatics** was initiated independently from the other group efforts. A brief overview of the activities of each Group in the Division, and highlights of several research programs, are given below:

Selected Program Highlights:
The **DNA Technologies Group** engages in DNA and molecular biology research to enhance measurement technologies in **mutation detection** and **genetic toxicology** and to provide Standard Reference Materials (SRM) for application in areas related to the detection and characterization of DNA. The Group has conducted interlaboratory tests that are designed to evaluate methods for DNA-based human identification on an annual basis. Standard Reference Materials have been developed to allow accurate characterization of DNA profiles for forensic and paternity testing. Completion of all interlaboratory testing occurred in 1997 for the **new SRM 2392 human mitochondrial DNA.** Activities in

FY98 completed validation and sequencing studies. Production of SRM 2392 is planned for completion in FY99.

Continued work with the **forensic testing** community led to development of a Web Site for **Short Tandem Repeats (STR)** information that includes a database of all currently used genetic testing systems. Use of STRs by crime laboratories throughout the world is rapidly becoming the preferred method of human identification. The Web Site (**STRBase, http://ibm4.carb.nist.gov:8800/dna//home.htm**) includes a comprehensive reference listing, a compilation of population statistical studies, a section for reporting rare genetic types, and a listing of researchers who have experience with STRs.

Long-range research in the Group includes the development of methods for detecting and quantifying **DNA damage and repair**, processes that are critical to the understanding of mechanisms of tumor initiation or tumor blockage. Methods have been developed to characterize DNA damage on a molecular scale at levels approaching one base per million using GC/MS techniques. These methods have been used to study the kinetics and specificity of DNA repair by newly discovered enzymes. In addition, treatments for cancer and other diseases, such as HIV, can result in collateral DNA damage to normal cells, including germ cells, that can then pass damaged or corrupted genetic instructions to future generations. Measurements of drug induced damage are being used to quantify cell death and DNA damage of individual and combined drugs for HIV treatments.

A workshop, **"Standards for Nucleic Acid Diagnostic Applications,"** was held at NIST, March 15-18, 1998, to determine what standards for nucleic acid diagnostics were needed by the emerging molecular diagnostics community. In addition to common and specific standardization issues, methods to assist these communities in their measurement capabilities and quality assurance, were addressed.

Finally, working in several areas of **molecular biology**, the Group is actively manipulating DNA to produce native and/or engineered enzymes with specific functions useful to the biotechnology community. These enzymes include a specific DNA polymerase derived from a thermophilic *Mycobacterium* for DNA sequencing. Thermophilicity is important since enzymes of commercial interest must work at elevated temperatures. Additionally, studies are ongoing to uncover mechanisms of adenyl cyclase modulation by catalytic site mutants of protein IIA in *Escherichia coli.*

The **Bioprocess Engineering Group** is focused on the development of measurement methods, databases, and generic technologies related to the use of biomolecules and biomaterials in manufacturing. Measurement methods and data have been developed in the protein **biospectroscopy** area that will lead to improved understanding of intra- and inter-protein electron transfer processes. This understanding helps industrial biocatalyst development through more efficient utilization of carbon sources (e.g., renewable resources) and nutrients, and in developing new ways to drive organic syntheses such as the stereospecific hydroxylation of pharmaceutical precursors. A new initiative to develop fluorescence intensity standards has also been launched this year in response to industry and government needs as reflected by the output from a workshop held at NIST.

In the **biothermodynamics** of enzyme-catalyzed reactions research area, chromatography and microcalorimetry measurements have been combined with chemical equilibrium analysis to develop thermodynamic data for several industrially important biotransformations. The metabolic pathway by which microorganisms and plants convert glucose to aromatic amino acids is a current focus of our biothermodynamic measurements. This chorismate metabolic pathway is under current investigation by several large chemical companies as an environmentally friendly source of aromatic hydrocarbons. In the **preparative bioseparations** project, electrochromatographic/electrophoretic separation equipment and methodology are being applied to the separation of different physical forms of DNA (supercoiled plasmid, relaxed circular plasmid, linear genomic). Large-scale purification of these materials is an emerging need in industries developing gene therapies and diagnostic materials.

Research projects in **biocatalytic systems** focus on enzyme characterization by site-directed mutagenesis, ^{15}N Nuclear Magnetic Resonance (NMR) spectroscopy, X-Ray diffraction of protein crystals and computational chemistry. These techniques are being used to address focused, industrially important biotransformation problems such as those found in hydroxylation and aromatic amino acid metabolic pathways.

Research in the **Structural Biology Group** at the Center for Advanced Research in Biotechnology (CARB) is focused in four key areas of industrial biotechnology. These include: macromolecular structure determination by X-Ray crystallography; molecular structure and dynamics elucidation by modern, high-field NMR spectroscopy; physical, molecular and cellular biochemistry; and computational biochemistry and modeling. A balanced program in these four areas has been developed at CARB by recruiting a highly interactive group of scientists through both University of Maryland Biotechnology Institute and NIST with interests and expertise in the theory and measurement of macromolecular structure-function relationships that underlie virtually all biological processes. In response to its distinct responsibility as part of a unique collaboration among NIST, the University System of Maryland and Montgomery County, CARB established close links in FY98 with several outside organizations. Examples of these relationships include a partnership with **The Institute for Genomic Research** (TIGR), the world leader in genomic sequencing of microorganisms, and with the largest biotechnology company in Maryland, **Life Technologies, Inc.**, who have endowed a faculty chair at the Center. Additionally, the CARB staff engaged in a range of technical activities that relate to NIST and CSTL's core mission in measurement science and chemical and process information.

The new, state-of-the-art laboratories in CARB IB were completed, equipped, and occupied in FY98. This much needed expansion of research space was celebrated at a symposium held on the Shady Grove campus on April 3-4, 1998, in conjunction with CARB hosting the annual meeting of the **International Network of Protein Engineering Centers** (INPEC) on April 4-7. Over 200 scientists from academic, government, and industrial laboratories attended the symposium, which focused on forefront issues in structural biotechnology. The new research space in CARB IB is accommodating the growing computational and biochemical groups at CARB. Additionally, the space will also temporarily be home to the new **Protein Data Bank**, which has been awarded to the **Research Collaboratory for Structural Bioinformatics**.

A new area of focus for the X-Ray crystallography and modeling groups has been the enzymes of the chorismate pathway. This effort is part of a Division-wide activity aimed at the vitally important industrial area of **metabolic engineering**. New structures for wild-type and mutationally-altered chorismate mutase have prompted a novel proposal from the modeling group for the chemical mechanism for the conversion of chorismate to prephenate. This hypothesis is subject to biochemical investigations, with the ultimate aim of the project to improve on the nominally low rates of the enzyme-catalyzed processes in the pathway. The NMR activities of the group have continued focusing on new methods for enhancing the sensitivity and resolution of heteronuclear, multiple resonance experiments applied to isotopically-enriched nucleic acids. These methods are of key importance to industrially crucial screening processes for high-affinity ligands that disrupt clinically important nucleic acid-protein interactions. Along these lines, the biochemical research of the group has continued to put descriptive, qualitative biochemical assays in a more quantitative, chemical framework. The mechanisms of transcription activation by prokaryotic enhancers are yielding to a combination of rigorous energetic approaches coupled with traditional biochemical assays. Contributions of the group to the area of chemical and process information stem from a new enterprise to construct a comprehensive database for molecular recognition. An initial area of focus, recommended by a distinguished panel of academic, government, and industrial scientists assembled at two NIST workshops, is on calorimetry data as applied to host-guest interactions.

The **Biomolecular Materials Group** is examining the underlying need for many applications of biotechnology by the control of biological molecules at interfaces. Chemically controlled surfaces engineered for specific biomolecular interactions are essential components of biosensors, bioelectronics, biocatalytic systems, and many diagnostic devices. **Biomolecular materials** thus influence such diverse applications as pharmaceutical development, health care, environmental pollution monitoring, and chemical manufacturing. A major focus of the group is a rugged artificial membrane system that mimics cell membranes. This **hybrid bilayer membrane** is composed of both artificial and natural lipid components, and is a unique membrane matrix that is both an excellent research tool as well as a commercially important development. Development of the chemistries needed to attach the lipids to a surface has been critical to the progress in this area. Fundamental understanding of the structural characteristics of biological molecules such as cell membrane receptors, optically active proteins and redox enzymes in this and other biomimetic matrices, and the relationship between structure and functional activity, are key to successful commercial applications. Molecular details are provided by **vibrational spectroscopies** such as infrared and surface plasmon resonance enhanced Raman, and by **nonlinear optical spectroscopies**. The development of models based on electromagnetic wave theory permitted the development of simulated spectra that aid data interpretation. Recent development of **infrared ellipsometry** has been useful for determining lipid orientation and conformation. Similarly, **neutron reflectivity** (in collaboration with the NIST Neutron Research Facility) is providing high-resolution data of these membranes and the location of protein complexes in them. Genetically engineered proteins such as pore-forming **α-hemolysin** are used in systematic studies of how membrane protein structural changes lead to functional changes. The development of stochastic models aid in interpretation of results and design of new experiments. **Sensor applications** development demonstrates the potential commercial usefulness of these proteins and matrices. Synthetic chemistry efforts are providing novel materials to allow assembly of matrices that are even better biomimetics. These tools need to be in place to permit assessment of the activity of biological molecules in high-throughput formats, and to allow the successful engineering, characterization, and application of biomolecular materials for development of future products of biotechnology.

In FY98 the Biotechnology Division initiated the establishment of a **Bioinformatics** program. This has involved recruiting new staff members and reassigning others to create a nucleus of people that will form the beginnings of the NIST program. This year's efforts have focused on interactions with scientists from Rutgers University, the University of California San Diego Supercomputer Center Rutgers, and the NIST Standard Reference Data Program to establish the **Research Collaboratory for Structural Bioinformatics** (RCSB). This organization provides a unique framework for the development of web-based resources (http://www.rcsb.nist.gov) of general interest to the academic, private, and industrial research communities. The strength of the organization is illustrated by the successful bid for the NSF/DOE/NIH funded **Protein Data Bank**. The RCSB will assume the responsibilities of managing and distributing the Protein Data Bank during FY99. This resource will be moved from its current home at Brookhaven National Laboratory to the sites of the three partners, NIST, Rutgers, and UCSD.

The dynamic nature of the biotechnology industry requires an evolving Biotechnology Division that necessitates strengthening existing programs and the development of technical expertise in new areas. The expansion of the DNA technologies effort to include measurement tools and quality assurance standards for **DNA diagnostic measurements** will continue to be a high priority in FY99 because of the rapid growth of industrial applications in this area. Included in Division plans are a broadening of the Biomolecular Materials Group's program to include an emphasis on generic needs common to many kinds of surfaces and materials that are components in sensors, processing, diagnostics and other applications. This is a reflection of the importance of biomolecular structures in the future development of biotechnology, particularly in pharmaceutical development and biomanufacturing. Additionally, expanded emphasis will be placed on the development of modeling that relates molecular structure to the properties of biomolecules, biomaterials, and bioprocesses. The use of biological macromolecules in non-biological applications such as **chemical manufacturing** and **environmental bioremediation** continues to be a promising area of biotechnology. The Division will continue to build expertise in bioprocessing technology, with an emphasis on measurements and data to help industry solve generic problems that limit technology development. For example, exploration of chorismate metabolic pathway engineering will continue to develop the information, measurement, and standards requirements for a new area of metabolic engineering. Fluorescent standard development for flow cytometry will also be a particular area of concentration. Continued expansion in the area of **Bioinformatics** is planned for the Division in FY99. This will include the development of computational methods for using large biomolecular structure and sequence databases to identify, analyze, or predict the structure and/or function of new biomolecular species. These expanded capabilities will enhance our Division's research programs and aid industry in the efficient use of chemical and biochemical data in the development of new products and processes.

Staff Recognition: This year several of the Biotechnology Division staff have been recognized for their achievements. **Ken Cole** of the Bioprocess Engineering Group was awarded the NIST Bronze Medal for the development of advanced technologies required for preparative-scale separations of different physical forms of DNA. He has developed the first use of electrochromatography for the isolation of large, fragile DNA molecules. The materials and methods developed by Dr. Cole preserve the molecular conformation and morphology of the DNA that are necessary to maintain the biocompatibility of the DNA with a targeted host. The technology will be used to obtain highly purified forms of plasmid-length DNA that can be used in a variety of biotechnology applications such as gene therapy or the development of new bioreactions and biocatalysts. **Barbara Levin** has been awarded the Department of Commerce Silver Medal for excellence in her guidance and management of committee activities that deal with research involving human subjects at NIST and at the Department of Commerce. While leading these efforts, she has also conducted research leading to the development of the first human mitochondrial DNA SRM to provide quality control in forensic identification, medical diagnosis, and mutation detection. Finally, **Kevin Ridge** was awarded the Karl Kirchgessner Foundation Prize for his pioneering work on the folding and assembly of integral membrane photoreceptor rhodopsin, a model system for drug receptors of immense biomedical importance. Rhodopsin is a prototype of a large family of G-protein coupled receptors sharing the seven-transmembrane helix structural motif. Despite the fact that more than half of the 500 targets for which the pharmaceutical industry has developed molecules that alleviate disease fall into this superfamily of receptors, little is known about their high resolution structures, nor about the processes whereby they adopt their active conformation *in vivo*. The Scientific Advisory Panel of the Foundation recognized Ridge's innovative work using state-of-the-art molecular biological, biochemical and structural biological approaches to understand the folding of rhodopsin.

B. Selected Technical Reports

1. *Short Tandem Repeat Database Implemented for Forensic Laboratories*

D.J. Reeder, J.M. Butler (Genetrace, Inc.), C. Ruitberg, and M. Tung

Objective: To support forensic laboratories with information on Short Tandem Repeats, the current method of choice for DNA-based human identification.

Problem: Although the FBI has chosen a set of thirteen core genetic loci for use in a national database (CODIS) of convicted felons, there was no convenient single web site to access information about the technology. Additional information on human identification was not organized in any coherent fashion.

Approach: The Web Site (STRBase, http://ibm4.carb.nist.gov:8800/dna//home.htm) includes a comprehensive reference listing, a compilation of population statistical studies, and a listing of researchers who have experience with STRs. An extensive update in FY98 increased the number of references to over 660 and added new features such as the DNA Advisory Board.

Results and Future Plans: Included in STRBase are facts and sequence information on selected STR systems, population data, a review of various technologies for STR analysis, and allele frequency distribution information. In addition, commonly used multiplex STR systems, PCR primers and conditions, a summary of validation studies performed on various STR loci, the FBI CODIS Core Loci, and NIST DNA-based Standard Reference Materials are discussed. Addresses for scientists and hyperlinks to organizations working in this area are included along with a new section for reporting rare genetic types. Future updates will include additional information on population data for each genetic system along with more details on DNA sequence patterns.

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2. *Cloning of PolI Gene from <u>Mycobacterium thermoresistibile</u>: Expression and Purification of DNA Polymerase I for Sequencing of G:C Rich Genomes.*

Madhavi Kamireddi and ***Prasad Reddy***

Objective: The aim of this research plan is to isolate DNA polymerase I from *Mycobacterium thermoresistibile* which can accurately and efficiently edit and polymerize its own chromosomal DNA, and to explore the utility of the enzyme for sequencing DNA with high G:C content.

Problem: Genomes of several microbial species including *Mycobacterium* contain a high ratio of about 70 % G:C to 30 % A:T. Consequently, deciphering the nucleotide sequence of these genomes and of the individual genes of these microbes is extremely difficult due to the formation of hairpin like DNA structures.

Approach: In order to address the problems associated with the sequencing of G/C rich genomes, the PolI gene from *Mycobacterium thermoresistibile* (Mth) was selected for cloning because its DNA contains 70 % G:C. After cloning the Mth PolI gene, the polymerase was overproduced in the pRE expression vector, purified to apparent homogeneity, and assessed for its use in DNA sequencing.

Results: The Mth PolI gene was cloned by Southern hybridization in two steps and the nucleotide sequence of the PolI gene was completely determined. The gene was subcloned into the pRE expression vector modified to code for the hexahistidine tag. The polymerase I was overproduced to about 25 % of the total cellular protein. Overproduced polymerase I was completely soluble. The enzyme was purified to apparent homogeneity on Ni-affinity resin and DEAE cellulose chromatography. Mth polymerase I was tested for processivity and its ability to sequence DNA templates. Mth polymerase I is a processive enzyme that in initial studies generates only about 200 bases of unambiguous DNA sequence.

Future Plans: Like most classes of polymerases I, Mth polymerase I also contains 5'-3' exonuclease domain and associated activity. This is probably the reason for obtaining as few as 200 bases in DNA sequencing. To test this hypothesis it is proposed to eliminate the exonuclease activity by site-directed mutagenesis of a critical tyrosine residue in the active site of the exonuclease domain. This modification would not alter the polymerization ability of the enzyme. To aid the protein engineering efforts, preliminary experiments are a prelude to three-dimensional crystal structure determination.

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3. Substrate Specificity of the Ntg1 and Ntg2 Proteins of Saccharomyces Cerevisiae for Modified Bases in Oxidatively Damaged DNA

__Miral Dizdaroglu__, Sema Sentürker, Patricia Auffret van der Kemp (France), Ho-Jin You (Emory University, Atlanta, GA), Paul W. Doetsch (Emory University, Atlanta, GA), and Serge Boiteux (France)

Objective: To develop methods for determining the repair specificity and excision kinetics of oxidative DNA base damage by DNA repair enzymes.

Problem: Oxidative damage generates a multitude of modified bases in DNA that are repaired by an array of repair enzymes. The biological role of newly discovered DNA repair enzymes is difficult or impossible to determine without knowing the damaged-base specificity. Current methods for determining this specificity have limited the progress in determining, the role of specific repair enzymes in biological systems.

Approach: A model system, comprised of two genes of *Saccharomyces cerevisiae*, *Ntg1* and *Ntg2*, that encodes enzymes with significant sequence homology to the *E. coli* enzyme endonuclease III, has been used to develop methods to assess specificity and excision kinetics. The two enzymes, called Ntg1 and Ntg2, have been determined to be DNA glycosylases that possess an activity for modified bases in oxidatively damaged DNA. An accurate measurement of DNA lesions is achieved by the use of gas chromatography/isotope-dilution mass spectrometry (GC/IDMS). The substrate used was calf-thymus DNA exposed to γ-radiation. Because of its ability to simultaneously measure a large number of DNA lesions, this technique permits one to study the repair of modified DNA bases. Substrate specificities of DNA glycosylases can be accurately measured using GC/IDMS. From these results, kinetic parameters were determined. Excision was measured as a function of enzyme concentration and time. This unique approach was used to determine the excision of a multitude of modified DNA bases Ntg1 and Ntg2 proteins from damaged DNA.

Results and Future Plans: Ntg1 and Ntg2 proteins were overexpressed in *E. coli* and purified to apparent homogeneity and analyzed as described above. The results revealed excision by Ntg1 and Ntg2 proteins of six pyrimidine-derived lesions, 5-hydroxy-6-hydrothymine, 5-hydroxy-6-hydrouracil, 5-hydroxy-5-methylhydantoin, 5-hydroxyuracil, 5-hydroxycytosine and thymine glycol. The Ntg1 and Ntg2 proteins also released two purine-derived lesions, 4,6-diamino-5-formamidopyrimidine and 2,6-diamino-4-hydroxy-5-formamidopyrimidine from γ-irradiated DNA. In contrast, Ntg1 and Ntg2 proteins did not release 8-hydroxyguanine or 8-hydroxyadenine. The results also show that kinetic constants varied among the different lesions for the same enzyme. The substrate specificity of Ntg1 and Ntg2 proteins was compared to that of other DNA glycosylases This revealed that Ntg1 and Ntg2 proteins exhibit a similar substrate specificity, but that this specificity is different from those of other DNA glycosylases studied thus far. This work will be extended to other DNA glycosylases such as those isolated from mammalian tissues including human tissues.

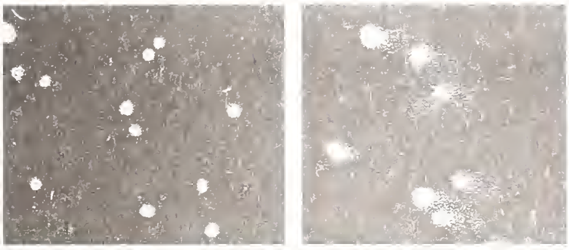
4. *Single-Strand DNA Breaks from Combined Therapeutic AIDS Agents*

B.C. Levin, J. Chen, and D.J. Reeder

Objective: To assess the use the Single Cell Gel Assay (Comet Assay) for measuring the DNA damage that occurs in human cells from individual and combined exposure to various recommended therapeutic AIDS agents.

Problem: DNA damage from adverse environmental exposures can lead to disease and cancer. If the damage causes mutations in germ cells, these adverse effects can be transferred to future generations. One indicator of such damage is the Single Cell Gel Assay that detects single-strand DNA breaks. Azidothymidine (AZT) has been noted to cause such breaks by other detection methods. If the sensitivity of the Single Cell Gel Assay allows detection of these breaks, then the assay could be used to determine the concentration of AZT and time of exposure that are required to produce such damage. Since current therapy for AIDS consists of combined chemical exposures, it is important to determine whether the combined exposures would produce more damage than the single exposures.

Approach: The Single Cell Gel Assay is able to detect single-strand and double-strand DNA breaks in individual eukaryotic cells; requires small numbers of cells (<20,000 per sample); can detect DNA damage from low levels of toxic or physical insults; and is rapid, simple, and efficient. In this assay, cells are 1) treated with the agent of interest, 2) embedded in agarose on a histological slide, 3) the cell membranes are lysed, and 4) the slides are placed in an electric field. If the DNA has single or double-strand breaks, it will flow out of the cells and move toward the anode, causing the cell and its DNA to resemble a comet. The more DNA released from the cell, the greater the DNA damage. A computerized imaging system is used to score and measure the comets. In this study, the therapeutic agents AZT, ddC and ddI were examined, both individually and in combination, to determine the amount of cell death and DNA damage.



Control Cells DNA Damaged Cells

Results and Future Plans: AZT produced single-strand DNA breaks, whereas ddC and ddI did not produce this type of DNA damage at the highest concentration tested. Examination of a concentration of AZT that produced minimal breaks in combination with either ddC or ddI enhanced the amount of DNA damage. The combination of all three therapeutic agents produced the greatest amount of damage. The Single Cell Gel Assay will be used to examine other compounds (therapeutic or toxicological) to measure the nature and type of DNA damage caused by these agents.

5. *A NIST Workshop on Standards for Nucleic Acid Diagnostic Applications*

C. D. O'Connell

Objective: To determine the standardization needs of the newly emerging molecular diagnostics community.

Problem: A result of the human genome project and rapid advances in molecular technologies is the focus on nucleic technologies in diagnostic testing. The DNA probe market has grown from around 20 million tests/year in 1990 to over 200 million in 1996. This market is projected to reach or exceed 5 billion tests conducted/year within the next 5 to 10 years. There is a significant need for consensus on standardization needs for this community. In the absence of national standards, individual laboratories have created their own. The informal sharing of ad hoc standards between laboratories leads to varying levels of accuracy of measurement betweem different laboratories.

Approach: From March 15 - 18, 1998 NIST held a workshop entitled "Standards for Nucleic Acid Diagnostic Applications". The workshop provided a forum for all of the communities that develop, conduct, or regulate molecular diagnostic assays in the areas of medical molecular genetics, infectious diseases and cancer. The workshop was organized to discuss both common and specific standardization issues facing the molecular diagnostics communities, and to arrive at a mechanism to assist these communities in accurate measurement capabilities and quality assurance for the wide variety of molecular tests conducted.

Results and Future Plans: Topics discussed during the meeting included: 1) the role of nucleic acid diagnostics in medical management; 2) the application of novel technologies; 3) the nature of nucleic acid standards for different molecular fields; 4) automation in nucleic acid analysis; and 5) current technologies and problems in the accurate measurement of repeated DNA that occurs with a variety of genetic diseases. Discussions of these topics by workshop participants resulted in the identification of the following areas of concern. First, the participants felt that a database containing information on the availability of reference standards, standard protocols, proficiency materials, and controls should be generated. Participants suggested that such a database could be generated by NIST and other Standards and Proficiency organizations such as the National Committee for Clinical Laboratory Standards (NCCLS) and the College of American Pathologists (CAP). Secondly, participants recommended that any SRMs generated should mimic the diagnostic test materials as closely as is possible. This will ensure usefulness of the SRMs for different diagnostic test platforms. Participants discussed specific standards needs and suggested that decisions concerning SRMs to be developed should be made jointly by NIST and the diagnostics community. The formation of a technical working group with membership drawn from industry, standards organizations, and government regulatory and non-regulatory agencies is being considered.

6. *Biothermodynamics Data for Industrial Applications*

***R. N. Goldberg**, Y.B.Tewari, and N. Kishore (Indian Institute of Technology, Bombay, India)*

Objective: To develop comprehensive data on the thermodynamics of enzyme-catalyzed reactions that can benefit biotechnology.

Problem: Knowledge of the position of equilibrium is essential for predicting the feasibility of chemical reactions and for the optimization of industrial processes. Reaction conditions such as temperature, pH, ionic strength, and cofactor concentrations can substantially affect the position of equilibrium of many enzymatically catalyzed biochemical reactions.

Approach: Chromatography, microcalorimetry, thermodynamic modeling, and the scientific literature are used as sources of thermodynamic data needed for assembling databases describing enzyme-catalyzed reactions. The microcalorimetric capability has been particularly important in allowing for the extrapolation of data to higher temperatures. This effort has also resulted in the development of estimation schemes based upon limited and carefully chosen sets of data.

Results and Future Plans: Recent research has focused on reactions in the chorismate metabolic pathway, which has been a focal point of interest because of its potential industrial importance. The thermodynamics of a major portion of this pathway have now been characterized by studying the reactions catalyzed by the tryptophan synthase, prephenate dehydrogenase, prephenate dehydratase, chorismate lyase, chorismate mutase, glutaminase, and tyrosine aminotransferase. In the case of two of these reactions, the thermodynamic measurements were complemented by quantum chemical calculations that used *Gaussian 94.* Thus, calculated values of absolute energies for the neutral and ionic species pertinent to these reactions both in the gas phase and in aqueous solution were obtained together with calculated structures and thermodynamic reaction quantities. The effects of water solvation and solvent polarization were accounted for by using continuum models. In the case of both reactions, there was a reasonable accord (difference ≈ 10 kJ mol^{-1}) between calculated and measured values of the enthalpies of reaction in aqueous solution. Thus, while the experimental values are still considered to be definitive, the relatively good agreement has served to lay a basis for the extension of quantum mechanics to other biochemical reactions. Plans are being made to complete the thermodynamic investigations in 1999 and thus obtain a relatively complete picture of the thermodynamics of this pathway.

Publications:

Tewari, Y.B., Kishore, N., Goldberg, R.N. and Luong, T.N., ***"An Equilibrium and Calorimetric Study of Some Transamination Reactions,"*** Journal Chemical Thermodynamics 30, 777-793 (1998).

Kishore, N., Tewari, Y.B., Akers, D.L., Goldberg, R.N. and Miles, E.W., ***"A Thermodynamic Investigation Of Reactions Catalyzed By Tryptophan Synthase,"*** Biophysical Chemistry 73, 265-280 (1998).

Tewari, Y.B., Chen, J., Holden, M.J., Houk, K.N., and Goldberg, R.N., ***"A Thermodynamic and Quantum Chemical Study of the Conversion of Chorismate to (Pyruvate + 4-Hydroxybenzoate),"*** Journal of Physical Chemistry B 102, 8634-8639 (1998).

7. *Preparative Bioseparations: Purification of Physical Forms of DNA*

***K.D. Cole** and C.M. Tellez (University of Illinois)*

Objective: To develop new high-resolution techniques to purify large amounts of different physical forms of DNA.

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

Approach: Electrophoresis has proven to be a highly successful method for the separation of nucleic acids on an analytical scale. Electrophoresis in gels and capillaries is a high-resolution analytical method, but scale-up is difficult. Electrochromatography (EC) is proving to be a promising method to scale up the electrophoresis of nucleic acids. EC is the application of an axial electrical field to a chromatography column. This research has been done in collaboration with Life Technologies, Inc. (LTI). LTI has provided a crude cellular extract that contained supercoiled circular DNA, nicked circular plasmid DNA (relaxed), linear genomic DNA (from host bacteria), RNA, and other cellular constituents. Another approach is gel electrophoresis with reversible media. Gel electrophoresis is another high-resolution technique that is not widely used as a preparative tool because of the difficulty of getting DNA or proteins out of the gel when the separation is achieved. The use of gel-forming polymers that change to solutions when the chemical environment is changed are being investigating. In collaboration with an investigator at the University of Illinois, a new technique is being developed that employs helical-flow free solution electrophoresis, which uses hydrodynamic as well as electrokinetic phenomena to induce separation.

Results and Future Plans: Electrochromatography was effective at separating the supercoiled plasmid, relaxed circular plasmid, and linear genomic DNA. The separation of different physical forms of DNA was determined by the electric field strength, the flow rate, and the porosity of the chromatography packing material. Plasmid DNA of variable molecular weight was size-fractionated by varying the electrical field strength. At a given electrical field strength and flow rate, lower molecular weight DNA plasmid fragments were not as strongly retained as higher molecular weight plasmid fragments. By selecting a specific set of conditions (packing material, flow rate, and electrical field strength) the molecular weight of DNA fragments retained by the column was adjusted. In the future, the behavior of very large DNA (such as bacterial artificial chromosomes) and small DNA (oligonucleotides) will be examined.

Publications:

Cole, K. D., ***"Concentration and Size Fractionation of Nucleic Acids and Viruses in Porous Media,"*** U.S. #5,707,850; Issued January 13, 1998.

Cole, K.D., ***"Preparative Separation of Plasmid and Bacterial Artificial Chromosome DNA by Density Gradient Electrophoresis in the Presence of Linear polymers,"*** Electrophoresis (in press).

8. *Biocatalytic System Analysis for Metabolic Engineering*

M.J. Holden, *M.P. Mayhew, A.E. Roitberg (GeoCenters), Inc., D.T. Gallagher, B. Coxon, N. Sari (CARB, University of Maryland)*

Objective: To develop measurement and modeling techniques for characterizing enzymatic transformations that are important to industrial applications of biocatalysis and metabolic engineering.

Problem: Many new metabolic pathways are being discovered and promoted for use in making chemicals from renewable resources (e.g., glucose from crop spoilage). The separate enzymatic steps in these pathways are not well characterized, as compared to the wealth of knowledge about pathways in mammalian cell physiology. Information such as biocatalytic rates, enzyme structure/function relationships, and genetic and allosteric control of reactant specificity is needed for successful bioprocess development, as judged on an industrial economic basis, to occur.

Approach: This activity uses molecular biology to engineer and produce proteins whose coordinated activity is then characterized and modeled by various measurement and computational chemistry techniques. Site-directed mutagenesis, NMR spectroscopy, and X-Ray crystallography/diffraction are used to determine and analyze molecular structure, while various molecular modeling techniques are used to interpret function.

Results and Future Plans: Two projects produce structural information on component proteins to model dynamic interactions during biocatalysis. One project deals with protein electron transfer. This biocatalytic system involves cytochrome P450 (CYP101) and its electron transfer partners putidaredoxin (Pdx) and Pdx reductase. In vivo, this Pseudomonad-based system derives reducing power from NADH. The P450 stereospecifically hydroxylates a variety of carbon-rich compounds and thus is of interest to both the chemical synthesis and bio-remediation industries. The intermolecular interactions are being investigating with regard to the flow of reducing power and exploring ways of engineering the system to reduce the need for cofactor regeneration.

The biosynthetic pathway leading from glucose to chorismate and its aromatic derivatives has major industrial potential and is another system under study. Through collaborations with industry and government laboratories, enzymology and structural investigations have been initiated on several key components that may be amenable to engineering for improved pathway throughput. A database that combines existing structural and other information with new measurements from the Biothermodynamics laboratory has been created. This metabolic pathway is being developed as a model system for bioprocess measurement and modeling technology.

Publications:

Roitberg, A.E., Holden, M.J., Mayhew, M.P., Kurnikov, I.V., Beratan, D.N., and Vilker, V.L., ***"Binding and Electron Transfer Between Putidaredoxin and Cytochrome P450cam (CYP101). Theory and Experiments,"*** Journal of the American Chemical Society 120, 8927-8932 (1998).

Sari, N., Holden, M.J., Mayhew, M.P., Vilker, V.L., and Coxon, B. ***"Exploration of the Structural Environment of the Iron-Sulfur Cluster in Putidaredoxin by Nitrogen-15 NMR Spectroscopy of Selectively Labeled Cysteine Residues," Biochemical and Biophysical Research Communications,"*** 249, 773-780 (1998).

D.T. Gallagher, Gilliland, G.L., Xiao, G., Zondlo, J., Fisher, K.E., Chinchilla, D., and Eisenstein, E., ***"Structure and Control of Pyridoxal Phosphate Dependent Allosteric Threonine Deaminase,"*** Structure 6, 465-475 (1998).

9. *Biospectroscopy: Applications and Standards Development*

***A. K. Gaigalas**, V. Reipa (UCLA), T. Ruzgas (Vilnius State University, Vilnius, Lithuania), G. Valincius (Vilnius State University, Vilnius, Lithuania), Li Li (William and Mary College), and V.L. Vilker*

Objective: Apply spectroscopic and electrochemical techniques to characterize biomolecular processes such as electrical or optical energy transfer between redox or fluorophore centers and external surfaces. Measure electron transfer rates and thermodynamic parameters associated with protein redox processes. Develop the scientific basis for producing viable fluorescence intensity standards.

Problem: Commercial application of redox enzyme biotransformations is hampered by the lack of data and models for intra- and inter-protein electron transfer, and by lack of inexpensive and reliable sources of reducing power. The application of fluorescence-based assays in biotechnology for purposes of tracking cellular genetic and metabolic activity has increased dramatically and further advances in the field are impeded by the absence of fluorescence intensity standards. This knowledge and data is important in the design/development of biocatalysts and biosensors.

Approach: Spectroscopic and electrochemical instrumentation such as linear sweep voltammetry (LSV), surface enhanced Raman spectroscopy (SERS), electroreflectance spectroscopy (ER), and spectroellipsometry (SE) has been developed. These techniques are being used to characterize electrode surfaces, to measure electron transfer in several redox proteins, e.g., putidaredoxin -- iron-sulfur redox center, azurin -- copper redox center, cytochrome c -- heme redox center, and to characterize the stability and quenching of model fluorophore-interface systems.

Results and Future Plans: The rate of oxidation/reduction of the heme group in cytochrome *c* (cyte *c*) when the protein is immobilized on a modified gold electrode was measured by high-sweep rate cyclic voltammetry, electrochemical impedance, and electroreflectance spectroscopy. The heterogeneous electron transfer rate coefficient, k_{het}, was determined from measurements by each method, and also from combining sets of simultaneous electrochemical impedance and electroreflectance measurements in a new impedance circuit for data analysis. All measurements were consistent with the view that the immobilized cyt *c* is retained at the electrode in the native state. Apparent k_{het} values, as determined by CV and by EI, are in relatively close agreement with each other (800 s^{-1}), but the values determined by ER, when interpreted using previously published methods are more than twice as large (k_{ER}= 2100 s^{-1} ± 300 s^{-1}). When measurements are analyzed for combined EI/ER data using a new impedance model containing a constant phase element, values of k_{ER} (400 s^{-1} to 800 s^{-1}) were in better agreement with the other techniques, but showed linear increase with frequency of ac modulating current. These values are among the highest heterogeneous rate constants measured for redox reactions of proteins immobilized at an electrode, and they begin to approach the rates of exchange between cyt c and its natural redox partner proteins. Further attempts to reconcile the discrepancies in k_{het} will focus on more detailed descriptions of the interfacial elements in the impedance models. Electrode surface tension measurements will also be developed using the surface charge modulation (estance) to elucidate the details of the protein interactions with metal and semiconducting surfaces, namely: electrode surface dipole moment, localization of the adsorbate, and lateral interactions between the adsorbed protein molecules.

Electromodulated fluorescence (EF) and electrochemical impedance (EI) measurements of fluorophores immobilized on modified gold electrodes showed that resonant energy transfer to metal states quenches the fluorescence of immobilized species. The distance dependence of this quenching is being used as a tool to study the dynamics of fluorophores at the interface. Future work will focus on measuring the surface density of immobilized fluorophores and changes in quantum yield induced by binding of antigens to the immobilized fluorophores.

Publications:

Gaigalas, A.K., Reipa, V., and Niaura, G., ***"Stark Spectroscopy of Ttryptamine Immobilized on a Gold Electrode,"*** Journal of Colloid and Interface Science 203, 299-310 (1998).

Ruzgas, T., Wong, L., Gaigalas, A.K., and Vilker, V.L., ***"Electron Transfer between Surface-Confined Cytochrome c and N-Acetyl Cysteine Modified Gold Electrode,"*** Langmuir (in press).

Reipa, V., Monbouquette, H.G., and Vilker, V.L., ***"Combined Spectroscopic Ellipsometry and Voltammetry of Tetradecylmethyl-viologen Films on Gold,"*** Langmuir (in press).

Henderson, L.O., Hannon, W.H., Vogt, R.F., Marti, G.E., and Gaigalas, A.K., ***"Terminology and Nomenclature for Standardization in Quantitative Fluorescence Cytometry,"*** Cytometry 33, 97-105 (1998).

10. Structural Metabolic Engineering: The 1.34 Crystal Structure of Chorismate Mutase

G. Gilliland, J. Ladner, and Andrew Howard (Illinois Institute of Technology)

Objective: To provide high-resolution 3D structural information for enzymes of potential utility in metabolic engineering. The structural data will be used as a basis for investigating the catalytic mechanism and regulation, data essential for developing effective models of metabolic pathways that can be used in developing and testing metabolic engineering principles.

Problem: Chorismate mutase from *Bacillus subtilis* is a central enzyme in the shikimate pathway that is responsible for the production of the aromatic amino acids and other aromatic compounds of commercial interest and hence a popular target for inclusion in metabolic engineering efforts. The chorismate mutase enzyme catalyzes the rearrangement of chorismate to prephenate that can then be converted to either tyrosine or phenylalanine. The enzyme provides a 2 x 10^6-fold rate acceleration over the uncatalyzed rearrangement. An earlier structure has been reported but the structure was carried out at medium resolution. Twelve monomers comprised the crystallographic asymmetric unit making it a difficult choice for investigating how its structure relates to function. A high-resolution structure of this enzyme is needed to provide the structural details for computational and modeling studies for investigating its function and developing engineering principles.

Approach: The crystal structure was determined at high resolution. First, crystals were grown by the method of vapor diffusion in hanging drops. Preliminary X-Ray diffraction studies revealed that the crystals belong to the space group $P2_12_12_1$ with the unit cell parameters a = 52.2 Å, b = 83.8 Å, and c = 86.0 Å. There is one trimer in the asymmetric unit. X-Ray data were collected at Argonne National Laboratory at the Advanced Photon Source on the IMCA-CAT beamline using radiation with a 1.0 Å wavelength. The crystal was held at 100 K and the intensities for 89,868 reflections to 1.34 Å were measured. The orthorhombic crystal structure was solved by molecular replacement using an earlier reported medium-resolution structure. Further refinement reduced the R-factor to 0.17 while maintaining good geometry.

The secondary structure of the chorismate mutase trimer.

Results and Future Plans: The final model shown schematically includes all 381 amino acid residues in the trimer, 8 sulfate ions, 5 glycerol molecules and 426 water molecules. This includes 32 residues that are modeled as having two conformations. The active site residues are well resolved. Surprisingly, the three active sites all contain a very tightly held and oriented sulfate ion and a glycerol molecule.

Preliminary analysis indicates that the sulfate and glycerol mimic the transition state of the substrate. The 13 C-terminal residues of each monomer stretch out and form hydrogen bonds with the residues in the active sites of crystallographic neighboring molecules demonstrating their flexibility and 'cross-linking' the crystals. This structure is now being used in the interpretation of how the structure of the active site relates to its catalytic properties. In this investigation residues are being selected for site-directed mutagenesis to test hypotheses concerning the enzymatic mechanism. Structures of these variants and the enzyme or variants complexed with substrate, products, and inhibitors will also be carried out to provide support for the mechanistic hypotheses.

11. Dramatic Enhancement of ^{1}H-^{13}C Correlated NMR Spectroscopy Using Multiple-Quantum Coherence Based Experiments

***J. P. Marino**, J. Diener (University of California-Santa Cruz), P. B. Moore (Yale University), S. Glaser (J.W.-Goethe Universität), and C. Griesinger (J.W.-Goethe Universität)*

Objective: To improve the sensitivity and resolution of ^{1}H-^{13}C correlations in nuclear magnetic resonance (NMR) experiments applied to uniformly ^{15}N,^{13}C labeled DNA and RNA oligonucleotides by generating multiple-quantum ^{1}H-^{13}C coherence during magnetization transfer and evolution periods in standard double and triple resonance experiments.

Problem: In solution NMR spectroscopy, the large one-bond heteronuclear ^{1}H,^{13}C and the geminal homonuclear ^{1}H,^{1}H dipolar interactions are the two chief mechanisms for relaxation of transverse ^{13}C and ^{1}H magnetization in ^{13}C-labeled macromolecules. As such, these dipolar relaxation mechanisms are the principle cause of decreased signal to noise and resolution in ^{1}H-^{13}C correlated NMR spectroscopy applied to ^{15}N,^{13}C labeled oligonucleotides. Proton, carbon multiple-quantum coherences, where all heteronuclei connected by single bonds are evolved simultaneously in the transverse plane, however are not affected by these strong dipolar interactions. Consequently, such coherences can be used to dramatically increase the transverse lifetimes, or T_2s, of these resonances and thereby improve the spectral sensitivity and quality.

Approach: In the slow tumbling limit characteristic of macromolecules, dipolar relaxation mechanisms are effectively 'switched-off' for multiple-quantum coherences involving the dipolar coupled nuclei. Consequently, ^{1}H,^{13}C multiple-quantum coherences should relax more slowly than the single-quantum coherences of the individual ^{1}H and ^{13}C spins. A strategy of using multiple-quantum line-narrowing is being employed to increase the sensitivity with which CH and CH_2 correlations are detected in the spectra of uniformly ^{13}C,^{15}N labeled ribonucleic acid (RNA) oligonucleotides. The strategy calls for using pulsed NMR techniques to generate ^{1}H,^{13}C zero- and double-quantum coherences for CH groups and triple-spin ^{1}H,^{1}H,^{13}C single- and triple-quantum coherences for CH_2 groups. The sensitivity and resolution improvements obtained using ^{1}H,^{13}C multiple-quantum coherence correlation are compared to equivalent single-quantum coherence correlated experiments. In addition, ^{1}H,^{13}C multiple-quantum coherence steps are incorporated into 'out and back' type triple-resonance NMR experiments currently used for through-bond assignment of RNAs, such as the ^{1}H,^{13}C,^{15}N (HCN) correlation

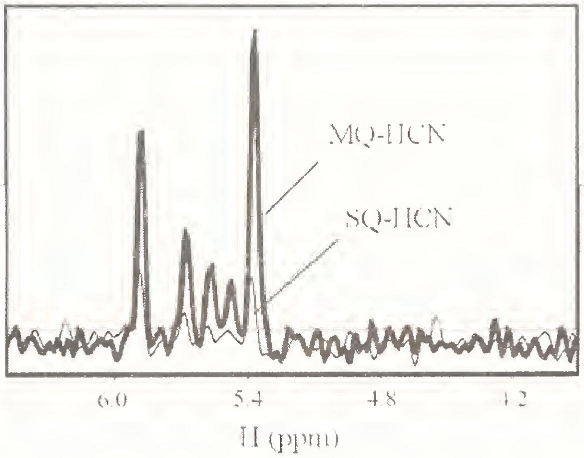


Figure 1: Comparison traces from HCN correleted spectra using multiple-vs. single-quantum cherence experiments.

experiment (see Figure 1) to further demonstrate the dramatic gains in sensitivity in practical applications.

Results and Future Plans: Using a 36 nucleotide RNA hairpin, sensitivity enhancements of up to a factor of three have been demonstrated for $^1H,^{13}C$ heteronuclear correlations for H1′,C1′; H2′,C2′; H3′,C3′ and H4′,C4′ methine groups and for H5′,H5′,C5′ methylene groups. These sensitivity enhancements were evaluated by comparing spectra obtain with 25 ms, multiple-quantum, constant-time, ^{13}C chemical shift evolution periods and spectra obtain with conventional 25 ms, single-quantum, constant-time evolution periods. In addition, an enhancement of up to a factor of five in sensitivity has been demonstrated by the incorporation of $^1H,^{13}C$ multiple-quantum coherence steps into 'out and back' type triple-resonance NMR experiments. In the future, this will be applied to a multiple-quantum coherence approach within the context of other triple resonance experiments used for RNA assignment. It will also be extended to studies of DNA oligonucleotides.

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12. Identification of the Regulatory Ligand Binding Site in Allosteric Threonine Deaminase

D. Chinchilla (CARB, University of Maryland), ***E. Eisenstein****, and F.P. Schwarz*

Objective: To design a variant of threonine deaminase to accelerate carbon flow into industrially important biosynthetic pathways by engineering amino acid substitutions into the enzyme that render it insensitive to the feedback modifiers isoleucine and valine.

Problem: A pressing problem facing biotechnology is to develop alternative approaches for the production of raw materials for *in vivo* chemical synthesis and bioprocesses. A particular bottleneck to the high-level production of key precursors for several chemical reactions in metabolism is the control exerted by feedback inhibition of allosteric enzymes, whose activity is regulated by the intracellular levels of biosynthetic end products. The adaptation of allosteric enzymes that were insensitive to feedback modifiers would alleviate precursor build up in cells and enhance biocatalytic pathways.

Approach: The approach to this challenge is to use protein engineering to manipulate the specificity or control of regulatory enzymes that regulate cellular biosynthetic pathways. Complementary information from structural, genetic, biochemical studies are used to construct new variants of allosteric enzymes with novel properties for specific use in metabolic engineering.

Results and Future Plans: Of current interest is pyridoxal phosphate-dependent, allosteric enzyme threonine deaminase. Specifically, information from genetic screens has been used to identify amino acid substitutions that disrupt the effects of the feedback regulators isoleucine and valine. These in turn are mapped onto the three-dimensional structure of the enzyme to identify the specific domain that binds the ligands. These data have provided a rationale for the construction of a feedback resistant variant of threonine deaminase that should increase the rates and yield and efficiency of certain end-products in branched-chain amino acid metabolism. Future work will focus on introducing the variants into cells for growth under specific conditions to assess their effects on three and four carbon α-keto acid biosynthesis.

Publications:

Chinchilla, D., Schwarz, F.P. and Eisenstein, E. ***"Amino Acid Substitutions in the C-terminal Regulatory Domain Disrupt Allosteric Effector Binding to Biosynthetic Threonine Deaminase from Escherichia coli,"*** Journal of Biological Chemistry 273, 23219-23224 (1998).

13. *Conformational Changes in the Seventh Transmembrane Helix of Visual Rhodopsin*

***K. D. Ridge** and N. G. Abdulaev (CARB, University of Maryland Biotechnology Institute)*

Objective: To identify regions in rhodopsin that undergo conformational changes upon light-activation.

Problem: The dim-light photoreceptor rhodopsin is a prototypical member of the superfamily of G-protein coupled receptors sharing the seven-transmembrane-helix structural motif that regulates a variety of sensory, hormonal, and neural responses. Rhodopsin is composed of the apoprotein opsin, a single polypeptide chain of 348 amino acids, and a covalently linked 11-*cis*-retinal chromophore. While the chemical aspects of rhodopsin structure have yielded to investigation, knowledge about the conformational changes that occur upon light-activation of the photoreceptor are far from being understood at the molecular level. The goal of this research is to understand signal transduction in the visual cell by localizing light-induced conformational changes in rhodopsin that trigger the binding and activation of G-protein.

Approach: Site-directed monoclonal antibodies were produced and used in order to detect and characterize conformational changes in rhodopsin. The antibodies were screened for their ability to recognize the protein exclusively in the light-activated state.

Results and Future Plans: Among several antibodies that showed light-dependent binding to rhodopsin, an antibody with the highest affinity ($K_a \approx 6 \times 10^{-9}$ M) was further purified and characterized. The epitope of this antibody was mapped to the amino acid sequence 304-311. This epitope extends from the central region to the cytoplasmic end of the seventh transmembrane helix and incorporates a part of a highly conserved NPXXY motif, a critical region for signaling and agonist-induced internalization of several biogenic amine and peptide receptors. In the dark state, no binding of the antibody to rhodopsin was detected. However, accessibility of the epitope to the antibody correlated with formation of metarhodopsin II, the physiologically important photointermediate in terms of signal transduction. Incubation of the antigen-antibody complex with 11-*cis*-retinal failed to regenerate the native rhodopsin chromophore. These results suggest significant and reversible conformational changes in the seventh transmembrane helix of rhodopsin that might be important for folding, assembly, and signaling.

14. Structure/Function Studies on the CC-CKR5 Receptor

K. D. Ridge

Objective: To identify the HIV-1 and chemokine binding sites on the CC-CKR5 receptor.

Problem: Various receptors for a class of proteins termed chemokines belong to the family of seven-transmembrane-helix receptors. Recent studies have shown that one of these chemokine receptors, CC-CKR5, acts as a "coreceptor" to mediate HIV-1 entry into various cell types. However, unlike rhodopsin and other seven-transmembrane-helix receptors, virtually no information exists about the chemical aspects of CC-CKR5 structure and function. The goal of this research is to map the HIV-1 and chemokine binding sites on the CC-CKR5 receptor.

Approach: Mutations that disrupt the binding site for HIV-1 but still allow chemokine binding are being introduced into a synthetic CC-CKR5 gene. The availability of a synthetic gene will make it possible to systematically express mutant forms of the receptor in order to identify structurally and functionally important regions of the molecule.

Results and Future Plans: A complete CC-CKR5 gene has been synthesized, assembled, and expressed in eukaryotic cells. Immunological assays indicate that CC-CKR5 is expressed at only about 20 % the level of rhodopsin when using an identical expression vector (≈ 2 µg CC-CKR5/ 10^7 cells *vs.* ≈ 10 µg opsin/10^7 cells). However, this level is sufficient for examining ligand binding using a filter-binding assay. The isolated CC-CKR5 protein shows two closely migrating species of ≈ 41 and 40 kDa. The reason for this difference in apparent molecular weight remains to be determined. Current efforts are focused on the chemokine binding studies, improving the levels of expression for alternative binding assays (such as surface plasmon resonance), and determining the extent of post-translational modifications on the receptor.

15. *Thermodynamics of Protein-Nucleic Acid Interactions*

***F. P. Schwarz**, S. Krueger (MSEL, NIST) and Y. Shi (CARB, University of Maryland Biotechnology Institute), and S. Wang (CARB, University of Maryland Biotechnology Institute)*

Objective: To determine the thermodynamic factors that control the binding of DNA to the α-helices of proteins using cAMP receptor protein (CRP) as a model DNA-binding protein and to determine if DNA binding to CRP is the control step in the activation of transcription by CRP in *Esherichia coli*.

Problem: Research on the thermodynamics of DNA-protein interactions has focused on the determination of binding constants using fluorescence tagging methods, gel-shift electrophoresis assays, and cellulose filter binding assays. Although these interactions are of fundamental importance in molecular genetics, little is known about the dependence of the binding constants on the enthalpy and entropy changes accompanying the binding reaction. Little is also known about how transcription activators such as CRP control the initiation of transcription *in vivo* as well as *in vitro.*

Approach: Isothermal titration calorimetry (ITC) was employed to determine the binding thermodynamics of DNA duplexes to CRP and its mutants. CRP is a 45,000 g/ mole dimer, consisting of a 3'-5' cyclic adenosine monophosphate (cAMP) binding site in the amino terminal domain and an α-helical DNA binding region in the carboxyl terminal domain. Upon binding of 3'-5' cyclic adenosine monophosphate to CRP, CRP binds specifically to over 20 different operons encoded for enzymes involved in carbohydrate metabolism to enhance their transcription by RNA polymerase in *Esherichia coli*. The DNA-CRP binding reactions involved in this study included three different DNA duplexes, each consisting of 41 base pairs, binding to CRP and to three mutants of CRP. T127L, S128A, and T127L/S128A, ligated to either cAMP , 3'-5' cyclic guanosine monophosphate, or 3'-5' cyclic inosine monophosphate. (The latter two cyclic nucleotides are analogues of cAMP.) The structure of the *lac* DNA operon 41 base pair fragment complexed to the cAMP-ligated CRP complexes was determined from small angle neutron scattering measurements (SANS). The results from binding of the *lac* DNA operon fragment to the cAMP-ligated CRP were compared to the amount of *lac* DNA transcripted to RNA in an *in vitro* transcription assay employing the complete *lac* operon as a DNA template.

Results and Future Plans: The DNA binding reactions were highly endothermic, from 60 kJ/mol to 150 kJ/mol, and, thus, entropically driven. The binding constants ranged from 5 x 10^6 L/mol to less than 10^3 L/mol and exhibit a high degree of specificity with regard to binding to the different CRP/ mutant complexes. The binding reactions between the duplex and the CRP/mutant complexes were observed to depend on the salt concentration, temperature, and the amount of D_2O in the buffer. The SANS measurements showed that the *lac* DNA fragment was bent in two turns around the cAMP-ligated CRP in solution, similar to the bending observed in X-Ray crystallography studies of the complex. This bending could account for the high endothermicity of the binding reaction. The amount of RNA produced in the *in vitro* transcription by CRP and its mutants complexed with the cyclic monophosphate nucleotides appears to correlate with their binding affinity to the *lac* DNA fragment, implying that DNA binding to CRP is the control step in the initiation of transcription by CRP. Further work will include determining how the magnitude of the DNA binding constant is controlled by the mutation in CRP and the thermodynamic role of RNA polymerase in transcription.

16. Structural, Kinetic, and Heteronuclear NMR Measurements of Enzyme-DNA Interactions: Models for Catalysis and Site-Specificity

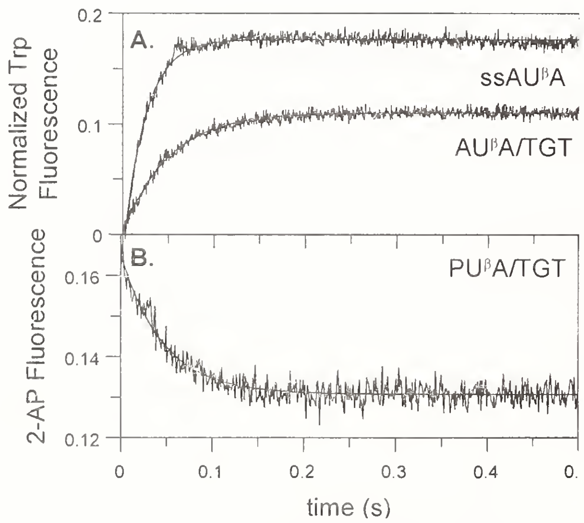
J.T. Stivers

Objective: To develop novel kinetic and NMR measurement methods that provide the basis for understanding the forces and interactions that lead to the large catalytic rate enhancements (10^{12}- to 10^{18}-fold) and specificities ($>10^6$-fold) of enzymes that act on DNA substrates. This work is intended to provide measurements and models that support the design of new drugs, and the bioengineering of improved catalysts for biotechnology and medical diagnostic applications.

Problem: Enzymes that act on DNA substrates have become powerful and indispensable tools in the current biotechnology revolution. These enzymes are used in medical diagnostic applications, the synthesis of novel reagents and drugs, and many basic research applications that ultimately lead to new biotechnology products. Thus, it is not an exaggeration to state that this revolution is *driven* by these enzymatic activities. Although Nature has provided many useful enzymatic activities without intervention by biochemists, it is highly desirable to develop methods and models that allow the rational design of new enzymatic activities. Such a goal is not trivial, and requires high-resolution structural methods, such as heteronuclear NMR and X-Ray crystallography, as well as new biophysical measurements that allow the characterization of unstable reaction intermediates and transition-states.

Approach: A comprehensive approach has been taken to obtain the highest level structural and mechanistic information on the prototypic DNA repair enzyme uracil DNA glycosylase (UDG). X-Ray crystallography, heteronuclear NMR spectroscopy, and rapid kinetic fluorescence methods are being used to unravel the detailed basis for the high specificity and catalytic power of UDG. The development of new measurement methods to understand the catalytic properties of UDG will provide general principles and technologies that should help us understand catalysis by other enzymes that alter the structure of DNA.

Results and Future Plans: The detailed mechanism by which UDG finds its target site in damaged DNA has been determined using stable fluorinated DNA substrate analogs in combination with fluorescence detection methods. This work, in combination with ultra-high resolution crystal structures of UDG, has allowed the construction of the microscopic steps that follow the initial encounter of the enzyme with the DNA. A key result of these studies is that specificity is *not* realized at the binding step, but instead, is derived from a conformational change in the enzyme and DNA that leads to stabilization of the transition-state. These results may provide a general explanation for how DNA repair enzymes recognize their specific damaged sites in DNA in any sequence context. The transition-state structure for the reaction is measured using isotope effect methods, and it is anticipate that it will be possible to design potent inhibitors of UDG that will be effective as antiviral drugs. The bioengineering of the active site of UDG to recognize different DNA bases is an additional future goal.



Fluorescence time courses for specific DNA binding and dissociation from UDG. The signals result from the enzyme (A) or the fluorescent DNA substrate (B).

17. Binding of Chorismate in the Active Site of a Mutant of Chorismate Mutase

*S. Worthington (CARB, University of Maryland Biotechnology Institute), **M. Krauss***

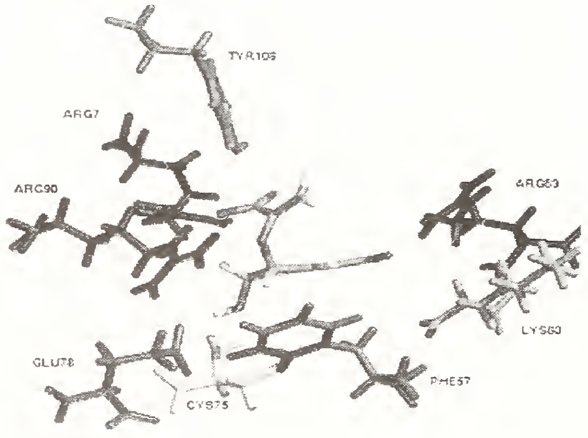
Objective: To theoretically modify the active site of an enzyme to predict structures and analyze the binding and reactive behavior for native and alternate substrates.

Problem: Determination of X-Ray structures of enzyme-substrate complexes relevant to the mechanism of reaction is dependent on the production of an appropriate crystal that is often difficult or impossible to obtain. Engineering the chemistry of the enzyme by mutating active site residues requires many structural determinations and thus, the production of numerous appropriate crystals. Theoretical methods are now being developed to determine active site structures for the modified enzyme starting from any native structure with a bound substrate relevant to the native chemical mechanism. The fundamental assumption is that the active site bound to the native substrate is relatively rigid. The active site binding of reactant, transition state, and product analogues can now be obtained where these molecules are optimized quantum mechanically. Also, selected mutant residues are optimized in conjunction with the reacting molecules. These procedures substantially leverage a single X-Ray structure into a wide range of relevant structures. These methods also allow the conservative modification of this active site into another with similar but not identical chemical behavior.

Approach: A powerful new method for calculating large molecular systems has recently been developed and is now being applied to biomolecules. The enzyme, for example, is divided into three regions, the chemically active substrate and residues, its immediate environment, and the rest of the protein. The first two regions constitute the active site of the enzyme. The chemical reaction must be treated quantum mechanically but even this smaller region can be too large for such a calculation to be tractable today. The chemically active region is treated by *ab initio* quantum chemistry while the immediate environment or spectator region is treated using effective fragment potentials (EFP) that represent the electrostatic, polarization, charge transfer, and repulsive interactions to the *ab initio* model.

The final outer region would be represented by charges for the electrostatic, polarization, charge transfer, and repulsive interactions to the *ab initio* model. The EFP integrals and gradients have been implemented in the GAMESS quantum chemistry code allowing optimization of the structures of the chemically active region in the immediate protein environment. The chemically active region can include protein residues as well as substrate molecules allowing the analysis of mutants as well as native structures. A wide variety of EFP's have been generated to represent protein residues including both the backbone and side-chain.

Results and Future Plans: Optimized structures have been obtained for chorismate, the oxabicyclic transition state analogue, and the product, prephenate both *in vacuo* and in the active site of chorismate mutase. The structure for the chorismate-enzyme complex can not be obtained experimentally and thus must be calculated (see figure). The glu78gln mutant has been calculated with the glutamine residue treated as part of the all-electron *ab initio* chemical complex with chorismate, the transition state analogue, and prephenate. Binding is predicted for the chorismate but the reaction will be inhibited. The reaction path will be calculated to investigate the enzymatic importance of the glu78 residue that can alter the path from the solution reaction. This technique can be applied to modified substrates and concomitant mutations to investigate the generation of new enzymes.



Chorismate mutase active site.

18. *Modeling Molecular Recognition and Conformational Flexibility*

M.K. Gilson, K. Mardis, and M.J. Potter

Objective: To develop efficient algorithms and software for computing the affinities of noncovalent complexes in solution.

Problem: The noncovalent association of molecules in solution is of fundamental importance in biology and chemistry. Software for predicting what molecules will bind each other, and how tightly they will bind, is needed by industry in order to avoid time-consuming and expensive binding measurements. Such software will be useful for designing molecules targeted to bind specific other molecules. Examples are drug molecules that work by binding enzyme active sites, and smaller host molecules that can be used for chemical separations. However, predicting binding affinities with sufficient accuracy and speed is difficult because of the complexity of the systems.

Approach: The approach has two main elements. The first is the use of simplified—and therefore computationally fast—treatments of the solvent that nonetheless capture much of the relevant physical chemistry. The utility of the generalized Born/Surface area model of the solvent is currently being explored. The second element of the approach is the use of a novel "mining minima" algorithm. This algorithm rapidly identifies the most stable conformations of a small-molecule system, and then computes the contributions of these conformations to the overall free energy. It combines an efficient energy-optimization method with careful treatment of the underlying statistical thermodynamics.

Results and Future Plans: The new approach has been applied to a series of small-molecule systems for which experimental data are available, and promising results have been obtained. The problems addressed include the association of organic ions in aqueous solution, the formation of ionic interactions between the charged side-chains of proteins, the association of nucleic acid bases in chloroform, and calculation of the conformational distribution of the drug-like molecule KNI-272. Based upon these studies, the method in its present form appears applicable to small molecules without flexible rings. However, further work is needed to apply the method to larger systems. In particular, the current algorithm cannot efficiently identify the low energy conformations of molecules with flexible rings. Methods of adding this functionality to the software are being studied, that use the macrocyclic molecule beta-cyclodextrin as a test case. Beta-cyclodextrin is of interest because it binds a range of small nonpolar molecules and is used by industry for a variety of applications.

19. Hybrid Bilayer Membranes as Cell Membrane Mimics: Structure and Function of Novel Tethering Chemistries

***C. Muese**, S. Krueger (Div. 856), A. Plant, and D. Vanderah*

Objective: A novel supported lipid bilayer, with a structure analogous to the membrane of living cells, is being investigated for its application as a rugged, biomimetic matrix for studying the structure and function of active membrane proteins. Novel lipids that tether the bilayer to a gold surface have been synthesized and investigated by infrared spectroscopy and by neutron reflectivity.

Problem: The cell membrane is the site of communication between the inside and the outside of the cell. It is a complex arrangement of proteins, lipids, and carbohydrates. An especially important class of proteins is cell membrane receptors, which are sites for control of cell metabolism, mobility, growth, and differentiation, and are important targets for new pharmaceuticals. Few experimental methods exist for studying the structure/function relations of these complex proteins, or for screening their activity. In previous work it has been demonstrated that the hybrid bilayer membrane (HBM) can provide a biomimetic matrix for membrane proteins and allow for their study using techniques such as vibrational spectroscopies, neutron reflectivity, surface plasmon resonance, electrochemistry, and other techniques. Since the proper structure and functioning of membrane proteins requires them to be associated with an appropriate lipid matrix, optimizing the composition of this stabilized membrane mimic is necessary.

Approach: HBMs consist of both natural (phospholipid) and synthetic (alkanethiol) components, are easily formed by self assembly, are supported on a conductive metal surface, and are stable for very long periods of time. These cell membrane-like materials are rugged enough and easy enough to fabricate that they have practical applicability to industrial-scale use. A series of novel compounds, thiahexa(ethyleneoxide)alkanes, have been synthesized to improve the ability to incorporate transmembrane proteins into HBMs. Based on previously published data it is expected that the ethyleneoxide moiety would provide a hydrated amorphous layer adjacent to the gold surface that would simulate an intracellular aqueous compartment. A series of novel tethering lipids have been synthesized and their structure investigated by infrared spectroscopy. In collaboration with the NIST Neutron Research Facility, neutron reflectivity has been used to examine the structure of HBMs containing this new chemistry and the effect of proteins on this structure.

Results and Future Plans: Surprisingly, reflection absorption infrared spectroscopy indicated that monolayers of thiahexa(ethyleneoxide)alkanes prepared by self-assembly are extremely well-ordered. Comparison to simulated spectra indicates a helical structure to the ethyleneoxide moiety and a crystalline packing arrangement in the alkane region. Since the infrared measurements are made in air, it is anticipated that neutron reflectivity measurements, which are made in water, might indicate a different structure. However, the neutron reflectivity results confirmed that the ethyleneoxide portion was unhydrated and well-packed. Even in the presence of melittin, a pore-forming protein, neutron data indicate that no water penetrates the ethylenoxide region. Future work involves modifying the fabrication methodology to prepare monolayers that consist of some thiahexa(ethyleneoxide)alkane molecules and some nonthethered lipid molecules. In addition, a new synthetic product, a thiahexa(ethyleneoxide) terminated phospholipid molecule is under development.

Publications:

Vanderah, D.J., Meuse, C.W., Silin, V. and Plant, A.L., ***"Synthesis and Characterization of Self-Assembled Monolayers of Alkylated Thiahexa(Ethylene Oxide) Compounds on Gold,"*** Langmuir. (in press).

20. Nanoscale Pore Forming Proteins: Structure and Function of a Prototypical Sensor Recognition Element

*D. Burden and **J. Kasianowicz,***
S. Cheley (Texas A&M), H. Bayley (Texas A&M)

Objective: To explore the ability of genetically engineered versions of the *Staphylococcus aureus* α-hemolysin (αHL) ion channel to serve as rationally designed sensor components for divalent metal cations and to deduce the molecular structure of channels when they are inserted into planar lipid bilayer membranes.

Problem: Alpha-hemolysin (αHL), a toxin secreted by the bacteria *Staphylococcus aureus*, self-assembles into a heptameric nanometer-scale pore in planar lipid bilayers. It thereby creates a conduit through which ions cross the membrane. Mutations can be introduced into the protein that result in specific ion binding and a subsequent alteration in the current flow through the channel. However, methods are needed to extract analytical information, such as ion concentration and identity, from the analyte-induced current changes. In addition, the tertiary structure of the protein pore in lipid bilayers must first be well understood, so that rationally designed mutants can be produced for a variety of measurement applications.

Approach: A combination of electrophysiology, genetic engineering, cell lysis assays, and optical methods are used to monitor the behavior of membranes containing single or multiple channels.

Results and Future Plans: Neither the hemolytic activity of the native αHL nor its single channel current are affected by aZn(II) concentration ≤ 1 mM, and binding sites for metal divalent cation can be created by altering the number and location of coordinating side chains between positions 126 and 134 inclusive. Although each of the single histidine substitution mutants for residues 129 through 134 inclusive, lysed rabbit red blood cells, 100 μM Zn(II) inhibited the hemolysis for only G130H, I132H, G133H, and G134H. Single channel current recordings of G130H exhibited conductance fluctuations whose frequency varied with the concentration and type of divalent cation. Although the αHL channel is comprised of seven identical monomers, the coordination of metal ions is not between 130H on different subunits. Specifically, a mutant containing G130H and in which the ionizable side chains adjacent to that site were replaced with non-coördinating counterparts (i.e. D127N, D128N, G130H, K131Q, and H144N) abolished sensitivity to Zn(II). Subsequent placement of a single aspartic acid into different positions in the latter mutant helped identify amino acid side chains, together with G130H, that comprise metal ion binding sites. Specifically, either D128 or G126D, but not D127, regained Zn(II) sensitivity to better than 1 μM. This finding suggests that the amino side chains alternate between pointing into and out of the pore and that the sites near position 130 span a reverse turn. Both conclusions are consistent with the recently determined crystal structure of native αHL in detergents. Future plans include modification of the channel to allow simultaneous multi-element detection.

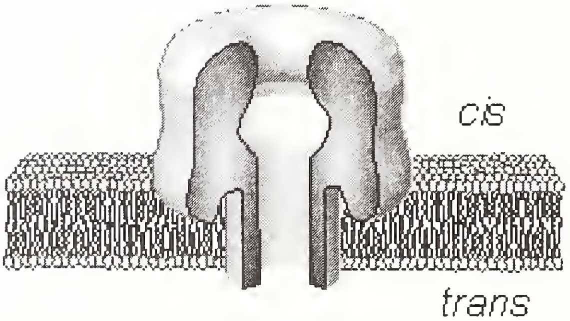


Figure 1. A representation of the α-hemolysin ion channel's crystal structure. The results of this study corroborate the pore's structure adjacent to the *trans* entrance.

Publications:
Kasianowicz, J., Burden, D., Han, L., Cheley, S., and Bayley, H., ***"Genetically Engineered Metal Ion Binding Sites on the Outside of a Channel's Transmembrane β-Barrel,"*** Biophysical Journal, 76 (*in press*).

21. Infrared Spectroscopic Simulations and Ellipsometry for Biomimetic Materials

C. ***Meuse*** *and A. Plant*

Objective: The purpose of this work is to improve the application of infrared measurements to the study of molecular orientation and conformation of organic thin films that are useful in pharmaceutical screening, biosensors, and other biotechnology applications.

Problem: Infrared spectroscopy is commonly used in biology, analytical chemistry, and materials science for the analysis of molecular structure. The interpretation of spectra is most often empirical, and most experiments only extract a small fraction of the available information. Simulated spectra based on electromagnetic wave theory provide a way of quantitating the molecular structural information contained in infrared spectra. The theory is mathematically complicated and currently used by only a handful of sophisticated spectroscopists. Wider application of the theory would allow quantitative analysis of the orientation and molecular composition of anisotropic samples; this capability will assist newly developing applications in pharmaceutical screening, biosensors, and tissue analysis and disease diagnostics.

Approach: An analysis module under a commercial mathematical software package is being developed for the simulation and interpretation of infrared spectra, based on a previously existing program that has not been widely used because of its complexity. The simulation relies on an initial reference spectrum and the application of the theory to predict quantitatively the effects that the composition, orientation, morphology and structure will have on the resulting spectrum. The program was validated using several reference materials and corroborative measurements including visible ellipsometry and neutron reflectivity.

Results and Future Plans: Using this program, the reflection absorption infrared spectra of alkylated 1-thiahexa(ethylene oxide) (THEO) self-assembled monolayers on gold surfaces has been simulated. The analysis indicates that the (THEO) portion of these compounds adopts the lamellar crystal morphology of polyethylene oxide in an ordered 7/2 helical structure and the analysis of the C-H stretching region shows that the alkyl tail is in a nearly *trans* extended conformation similar to normal alkanethiols. By simulating the RAIRS (reflection absorption IR spectrum) of a suspected structure using the program, it was determined that the correlation of the experimental and simulated spectra did not change with changes in the twist and azimuthal angles. This indicates that the THEO segment of the SAM is uniaxial with the helix oriented normal to the surface (0° ∀ 2°). The simulated results in the C-H stretching region are consistent with a tilt angle of 32° ± 2° to the normal of the substrate, similar to that found for other long chain (> C_{11}) n-alkanethiols and a twist angle of -30° ± 2°. The orientation of the lipid acyl chains has been determined to be 34° ± 2° in the alkanthiol-phospholipid hybrid bilayer construct. Future efforts include making the analysis package widely available to the infrared spectroscopy community and utilizing it to design experiments to study liquid/solid interfaces.

Publications:

Parikh, A.N., Allara, D.L., "**Quantitative Determination of Molecular Structure in Multilayered Thin Films of Biaxial and Lower Symmetry from Photon Spectroscopies.**" I. Reflection Infrared Vibrational Spectroscopy," J. Chem. Phys. 1992, 96, 927.

Vanderah, D J., Meuse, C.W., Silin, V., Plant, A.L. "**Synthesis and Characterization of Self-assembled Monolayers of Alkylated 1-Thiahexa(ethylene oxide) Compounds on Gold,**" Langmuir 1998, 14, 6916.

Meuse, C.W., Krueger, S., Majkrzak, C.F. Dura, J.A., Fu, J., Connor, J.T., Plant, A.L. "**Hybrid Bilayer Memebranes in Air and Water: Infrared Spectroscopy and Neutron Reflectivity Studies,**" Biophysical J. 1998, 74, 1388.

22. Computer Simulation Studies of the Energetics and Dynamics of Biomimetic Membranes

J.B. Hubbard, V. Simmons (CSTL Graduate Fellowship Program Awardee), J.C. Rasaiah (Univ. of Maine), R.D. Mountain (Div. 838)

Objective: Construct a statistically reliable equilibrium classical molecular dynamics simulation of surface-tethered alkane chains in contact with a realistic aqueous molecular environment. Extract thermophysical, spectroscopic, and dynamic information that then can be related to experimental and numerical modeling studies.

Problem: A system consisting of several hundred surface-tethered complex hydrocarbon molecules in contact with several hundred water molecules requires temporal resolution at the femptosecond time scale and a careful consideration of how to deal with the long range forces due to the presence of the electrical charge that resides in current models for molecular water. Nanosecond time-scales are typically required for equilibration while elaborate time-consuming numerical treatment of superimposed Coulomb potential effects can severely tax the capabilities of modern computational facilities.

Approach: An idealized description of the surface-alkane chain interaction along with a united atom, rather than a fully atomistic, representation of the intra- and inter-molecular forces has been adopted. In addition, selected spectroscopic features, such as C-H vibrations in the terminal methyl groups, have been incorporated for the purpose of establishing direct contact with infared experiments and phenomenological numerical modeling. In order to reduce simulation time and processor requirements, a thoroughly tested point charge model for water has been introduced with the additional simplifying feature of a finite-range cut-off in the Coulomb potential. This simulation of a composite surface-alkane chain - aqueous system is currently in the process of being fine-tuned. In order to accelerate the approach to equilibrium, a modular alkane chain- aqueous phase annealing procedure has been devised in place of more conventional global equilibration techniques.

Results and Future Plans: A system comprised of 225 sulfur-terminated, surface-tethered, seven carbon- atom alkane chains has been simulated over a range of temperatures and surface packing densities. Relative to the flat surface, atomic number density profiles, orientation distribution profiles, potential energy density profiles, and atomic level stress profiles have been obtained with a high degree of statistical reliability. Moreover, C-H relative velocity correlation functions for the terminal methyl groups have been calculated, normal and surface-parallel projections have been extracted, power spectral densities of these infrared active vibrations have been computed, and certain key spectral features have been fine-tuned so as to approximately match experimentally determined selected inferred features. A finite-range, point-charge based model for water consisting of about 500 molecules has been introduced into a 50-molecule, surface tethered alkane chain system, and several procedures designed to accelerate equilibration are currently being tested.

Future plans include the possibilities of carboxylating the terminal methyls, the introduction of hydrophilic spacers such as ethylene oxides into the alkane chain interior, the introduction of mono- and even divalent cations and anions into the aqueous-hydrophobic environment, the introduction of electrical fields, and the determination of electrochemical potential profiles together with the simulation of the dynamic electrical impedance response.

Publications:

Mountain, R.D. and Hubbard, J., ***"Molecular Dynamics Simulation of Tethered Chains,"*** NISTIR 6150 (1998).

III. Process Measurements Division (836)

Gregory J. Rosasco, Chief

A. Division Overview

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

Programs:
Process and quality control and equity in commerce ultimately depend on the accuracy of measurements. This generally requires calibration of instruments against, or use of procedures assuring traceability to, reference standards. Therefore, **measurement standards and calibration services** are a very major part of the Division's activities. We provide support critical for **temperature, humidity, fluid flow rate, pressure, vacuum, gaseous leak rate, liquid density and volume, and air speed measurements** with close to 1000 standard tests and calibrations performed each year. The Division's commitment to provision of these services involves many facets:

- the establishment, maintenance, and improvement of the primary standards;
- continuing comparisons of these standards with those of other nations;
- development of suitable mechanisms for transferring the requisite measurement accuracy to customers in the field and in secondary calibration laboratories; and
- continual attention to service efficiency and measurement quality.

While these measurement and calibration services are provided to a wide range of customers, we also have measurement support programs focused on specific strategic technologies, such as maintaining U.S. leadership in semiconductor device manufacturing. As part of NIST's National Semiconductor Metrology Program (NSMP), the Division is selecting, developing, evaluating, and validating **process measurement technologies important in semiconductor manufacturing**. These efforts include:

- provision of improved thermocouples for control of thermal processing equipment, including rapid thermal processing (RTP) systems;
- low-range gas flow standards; evaluations and models of the performance of residual gas analyzers used to monitor gaseous composition in fabrication tools;
- methods to determine plasma electrical properties;
- and very low-level water measurements for contamination control in process gases.

In some of these efforts, we make use of a reference processing reactor prototypical of industrial manufacturing. This allows critical tests of the measurement approach and its utility for the intended application. Because processing systems are complex, with strongly coupled chemistry and mass transport and electrical characteristics, reference reactors are subject to extensive modeling and validation efforts as an integral part of the measurement support activity. These models and supporting data play a critical role in the Semiconductor Industry Association's (SIA) National Technology Roadmap for Semiconductors (NTRS). In fact, modeling is specifically identified not only as a "crosscutting technology," but as "pervading all crosscuts". Our program in this area, partially supported by the NSMP, seeks to develop and validate **benchmark chemical mechanisms and supporting thermochemical and kinetic data, for equipment and process design and control**.

The technical approach described above, which emphasizes measurement technology development, provision of process models and supporting data, and validation on prototypical systems, characterizes not only our semiconductor-related efforts, but also is representative of our process-technology-related research in the areas of materials chemistry, spray combustion, and supercritical fluid processing. The first of these, highly synergistic with the semiconductor models and data program, develops **chemical and process models and data to support the production of high technology materials**. We have studied the use of sodium/metal halide chemistry to synthesize metal and non-oxide ceramic films, e.g., SiC, required for high-temperature, high-durability applications in industry. This novel processing method offers a relatively low temperature (low energy consumption) route with promise for bulk synthesis of these generally difficult-to-prepare materials. It also has the advantage of essentially zero-emissions, providing an inherently "green" processing approach for the production of high technology materials.

Addressing industrial problems associated with the operation and design of thermal reactors is the main focus of the Division's other programs in process technology. Based upon a unique combination of spray measurement capabilities and a laboratory-scale prototype spray combustion facility, the spray combustion program emphasizes measurement of the role of droplet dynamics (generation, transport, and mixing) in determining the performance (efficiency and emissions) of spray-based energy production and waste destruction systems. The primary objective of this effort is to **provide benchmark data for the validation of computational models for spray combustion and to establish a means to correlate performance with operating conditions**. Supercritical fluids are becoming increasingly important in modern technologies for precision cleaning, chemical synthesis and extraction, and as alternate working fluids in heating and refrigeration equipment. The large changes in fluid properties with temperature and pressure characteristic of fluids near their critical point lead to fluid flow and heat transfer fundamentally different from that in liquids and low-density gases. We are studying these fundamentals in supercritical fluids to develop and validate predictive models and computational fluid dynamic simulations required for process design and control.

The Division has a significant effort in the area of chemical sensor technology with two research programs: **micro-machined gas sensor arrays** and **diagnostic applications of self-assembled monolayers (SAMs)**. The first effort is collaborative with the Semiconductor Electronics Division of the Electronics and Electrical Engineering Laboratory. The technology is based on 'micro-hotplate' arrays comprised of CMOS-fabricated SiO_2 bridge structures formed by silicon micro-machining. Chemical sensors are fabricated by depositing metal oxides, e.g., SnO_2, and surface-dispersed catalytic metal-additives on the micro-hotplate to form robust, electrical-conductance-based sensing elements. Because of their small mass and consequent millisecond thermal time constants, these platforms enable temperature programmed sensing (TPS) that can lead to enhanced sensitivity, selectivity, and repeatability of the sensing response. Combined with properly selected metal oxides and catalysts, TPS arrays offer excellent potential for real-time sensing of multi-component gas mixtures. The objectives of our effort are to develop the knowledge-base required to optimize multi-species detection and quantitative analysis and to resolve generic device-processing issues which could limit commercial application.

Alkanethiol monolayers, of the general formula $X(CH_2)_nSH$, self-assembled on the surfaces of noble metal substrates are the second focus of the Division's sensor program. SAMs are robust, reproducibly prepared structures with highly tunable surface properties and serve as a model system for the study of many sensing applications. An example is DNA microchip technology, which has potential application in the areas of disease detection, toxicology, forensics, industrial processing, and environmental monitoring. Our research currently is focused on the self-assembly of DNA monolayer films on surfaces, with the goal to understand how the molecular surface structure of the DNA probes impacts the performance of the microchip devices.

A new program in process analysis was initiated this year. Joint with the Analytical Chemistry and Surface and Microanalysis Science Divisions, this research seeks to develop **frequency and intensity standards for Raman spectroscopy**. While recent breakthroughs in instrumentation hold promise for very widespread application of Raman analyses in industry, lack of these standards is a major barrier to its full deployment.

Selected Program Highlights:

The Division maintains and disseminates the International Temperature Scale of 1990 (ITS-90) over the range 0.65 K to 1235 K. Having completed the NIST realization of the scale in terms of its fundamental definition, our current activities are directed primarily at comparisons of realizations of the scale with other national measurement institutes and examination of the internal consistency (uniqueness) of the scale. We also continue work, joint with the Physical and Chemical Properties Division and the Optical Technology Division (Physics Laboratory), to improve the accuracy of thermodynamic temperature measurements above 500 K. Comparisons of standards are being carried out in two arenas. The first, under the auspices of the Consultative Committee on Thermometry (CCT) of the CIPM, involves four key-comparisons in the region 0.65 K to 1235 K. NIST is participating in all, coordinating laboratory for one, and regional sub-coordinator for another. Additionally, we have supplied the fixed-point cells and reference thermometers for another key comparison. We are also developing plans for extending some of the key comparisons to laboratories within the Interamerican Metrology System (SIM).

The Division provides the national standards and calibration services for pressure and vacuum measurements over 16 decades of pressure, from 10^{-7} Pa to 10^{9} Pa. As in the temperature standards area, international comparisons have grown in importance with NIST participating in six key comparisons dealing with pressure and vacuum standards. These are organized under the Consultative Committee for Mass and Related Quantities of the CIPM. We are leading, i.e. serving as pilot laboratory, three of these comparisons. These are sub-atmospheric and vacuum comparisons that have required NIST to develop totally new transfer standards, instrumentation, and protocols. Additionally, we are conducting a multi-laboratory comparison for near-atmospheric-pressure measurements within SIM. The latter program, with representatives from five regions within SIM, has involved a multi-day training program at NIST, visits by NIST staff to each participating laboratory, and, in some cases, equipping the participant with a reference standard and peripheral equipment.

In the fluid transfer measurements area, the Division provides gas flow and leak-rate standards and calibrations over the range from 10^{-14} mol/s to 10^{2} mol/s and similar services for liquid flows in the range from 10^{-3} L/s to 10^{3} L/s. To support measurement needs in industries such as semiconductor manufacturing, new high accuracy primary standards for low range gas flows are under development. Additionally, a series of ultra-stable, laminar flow elements have been developed for flows over a range of 10^{-7} mol/s to 10^{-3} mol/s. These instruments have demonstrated stability over the course of three years of ±0.1 % and have been used by NIST personnel to conduct on-site tests of industrial primary flow standards at over 20 facilities during that time. We have initiated a new, multi-year effort to upgrade our primary standards for gas flow measurements in the range 10^{-3} mol/s to 10^{-1} mol/s (1-100 standard liters per minute). Industrial needs and commercial instrumentation are rapidly moving toward higher accuracies, at or better than 0.1 %. A number of NMIs provide calibrations in this flow range with uncertainties under 0.1 %. Our effort has a dual goal, first to reduce the uncertainty of our primary standard to 0.05 % or less (k=2) and, second, to incorporate modern control and measurement instrumentation that will support automation and lead to higher accuracy, lower cost, and reduced turn-around time for these calibration services.

In another new project, we are seeking to extend the range of gas flow conditions for which NIST provides traceable calibrations. The project addresses ranges of very large flow rates, often at high pressures, and sometimes involving gases other than air, e.g., natural gas. This innovative new project will take advantage of existing calibration facilities at laboratories outside of NIST, e.g., secondary calibration laboratories within the U.S. or at other NMIs. This program will exploit modern communication networks to allow NIST presence at, and operation of, the external facility via tele-presence. We have formed collaboration in this effort with researchers at the NIST National Advanced Manufacturing Testbed within the Manufacturing Engineering Laboratory. Another novel aspect of this project is the development of an in-line ultrasonic travel-time flowmeter that will reside in the external calibration facility. This meter, again accessed and operated via the high-speed communications link, will provide real time information on the distribution of the flow entering the meter under test and serve as a check standard for the primary flow standard used in the calibration. This project, in its early stages of research and development, holds promise for a new paradigm for (flow) calibrations, for comparisons of primary facilities, and for accreditation of calibration laboratories.

Increasingly, industry is turning to NIST for flow calibrations for reactive and/or corrosive gases (e.g., for semiconductor manufacturing applications), for gas mixtures, and for gases at elevated temperatures (the latter two conditions are important in combustion and for automotive applications). Our current efforts to address these needs include the development of new metering technology, e.g., an acoustic Doppler-shift flowmeter, and the provision of new calibration facilities, i.e., the Heated Gas Mixture Flow Facility (HGMFF). The Doppler-shift flowmeter can be applied to any gas, requiring only conventional gas handling hardware for its construction and knowledge of the gas density near room temperature and one atmosphere pressure, i.e., nominally ideal gas conditions. The HGMFF provides variable composition (high concentration mixtures of air, N_2, CO_2, H_2O, and additions of one or more low concentration species), variable temperature (to 700 K) flows in the range 1 L/s to 36 standard L/s ($\cong$ 0.04 mol/s). This new facility has continued to be very important in testing a number of prototype meters being developed for the U.S. automotive industry as part of its push to ultra low emission vehicles. We interact directly with commercial meter manufacturers who are attempting to meet meter performance specifications set by the American Industry/Government Emissions Research consortium.

Also in the fluid flow area, research continued under a CRADA, involving five meter manufacturers, to investigate the use of non-intrusive ultrasonic flowmeter technology for improved accuracy in industrial measurements, such as in power plants. Results reported this year from testing clamp-on ultrasonic devices demonstrated precision of the order of 1 % or less in many cases. Also, it was shown that there is the need to address biases in the methods used to calculate average flow rates from the time-of-transit information. The promise of ultra-sonic multi-path flowmeters to provide accurate (primary) measurement of pipe flow has been studied both theoretically and experimentally for the past few years. Measurements with an uncertainty (k=2) of the order of 0.2 % appear to be achievable with today's technology. Computational simulations of flow measurement devices and their environments play an increasingly important role in the assessment of all our flow measurement standards. Refinement and validation of computational tools for both incompressible and compressible high Reynolds number (turbulent) flows, which are characteristic of many of our applications, is an important part of the overall program plan. This work has the vision of developing portable, scaleable primary flow measurement standards. These could play a vital role in establishing flow traceability within the U.S. and flow measurement comparability internationally.

A major thrust in the Division is to develop species-specific partial-pressure measurement methods and standards, which has major implications for both our humidity and vacuum standards program. In the humidity area, the goal is to extend primary measurements to lower ranges of concentration, i.e. from 10's of micromol/mol to tenths of nmol/mol, and to host gases other than air, e.g., process gases. We seek to extend vacuum metrology beyond the traditional inert gases to include identification and quantification of low-level (reactive) contaminants, even in higher-pressure background gases. Such contaminants play a critical role in determining the quality of vacuum-processed components, e.g., semiconductors, and represent a major challenge from the point of view of real-time process monitoring and control. Our current focus is on an optical measurement technique, cavity-ring-down-spectroscopy, which holds promise for measurements of water in vacuum, perhaps down to the 10^{-8} Pa range, and for ng/g of water in gases. Building on our previous theoretical and experimental studies, we have identified three critical elements for success in this effort:

1) the need for a versatile narrow-bandwidth frequency-stable light source,
2) the use of length-stable ring-down cavities, and
3) the excitation of single TEM cavity modes to obviate mode-beating effects.

Significant progress has been made in realizing these requirements. Individual cavity-ring-down times have been measured with a standard deviation as small as 0.02 % (within a factor of 4 of the theoretical shot-noise limit) corresponding to absorption at the level of approximately 10^{-10}/cm in a 10 cm cell. This translates to a partial pressure of water (measuring at an excitation wavelength of 1.4 μm) of 10^{-6} Pa ($\approx$10 pmol/mol) which could be determined with an imprecision of 0.3 %.

We continue to see significant progress in many areas of our research in support of semiconductor manufacturing. We have completed determination of a reference function for Pt/Pd thermocouples (TC). This TC has remarkable high temperature performance with stability of ±20 mK for temperatures up to 1200 K and ±100 mK for temperatures up to 1775 K. These TCs are undergoing tests in semiconductor manufacturing which requires very accurate temperature control in wafer processing furnaces. We also are developing the Pt/Pd couple, and other noble metal systems, as thin-film thermocouple thermometers to enable accurate surface-temperature measurement in RTP systems used in semiconductor manufacturing. A new reference thermal chemical vapor deposition (CVD) reactor was commissioned this year. Its initial application is a test of a recently developed chemical/transport model focused on understanding and controlling micro-contamination. The newly developed model includes realistic chemical kinetics in addition to (the more typical) energy and mass transport. It also contains a model, drawn from our work on nanophase materials chemistry, which accounts for the formation, transport, and coagulation of particles in the reactor. In the plasma processing area, we continue to develop models that describe the relationship between externally measured voltages and currents and the characteristics of the plasma, such as ion currents and energies, which are critical to processing. Validation of aspects of these models this year has utilized planar laser induced fluorescence (PLIF), a technique first developed for this application in our Division. We have begun an investigation of the use of residual gas analyzers (RGAs) as control sensors in a commercial semiconductor-processing tool. This work builds on previous development of a phenomenological model for the performance of RGAs. This model guides selection of operating parameters to reduce non-linear response and to mitigate the dependence of RGA signals on the pressure of background gases. Also, at the request of the SIA, we have assisted in the preparation of national and international standards of practice and measurement of perfluoro-compound (PFCs) emissions from processing reactors.

Significant portions of the database on the benchmark spray combustion facility were completed this year. The measurements completed thus far include concentration, size and velocity distributions of fuel droplets and quantitative gas phase concentrations. These measurements have been made within and at the exit of the combustor for a methanol spray flame. Temperature profile measurements have been initiated and heat flux measurements also are planned. Our industrial partners will use these data and sub-models to test models used for design and control of multi-phase combustors.

In the program to provide key engineering performance data on mass and heat transport in supercritical fluids, we completed heat transfer measurements for supercritical carbon dioxide flowing under conditions similar to those experienced in heat exchangers used in refrigeration applications. Anomalous enhancements and degradations in heat transfer efficiency were observed depending on closeness to the critical point and magnitude of heat flux. A correlation that accounted for all the observations also was demonstrated.

Recent improvements in device design and fabrication have resulted in enhanced reproducibility and performance of the micro-hot plate sensor array platforms. Reliable electrical contact to the sensing films is now achieved routinely and these contacts operate successfully for long times without degradation for typical thermal cycles. Chemometric signal analysis techniques were applied successfully this year to recognize and quantitate a binary mixture (A+B) on the basis of a calibration done with A and B individually. Decreases in sensor-sensitivity, presumably associated with degradation of the catalysts after long (>24 hours) high-temperature exposures to organic compounds, were discovered this year and are now under investigation. Also, new projects to explore specific applications of the sensor platforms are underway with industrial CRADA partners and other government agencies.

This year we made a rigorous determination of the structure of DNA-functionalized SAMs by measurements of neutron reflectivity. In this work we established that the surface conformation and activity is controlled by the self-assembly protocol used. We have also quantified the surface density of DNA immobilized on gold. The technique of chronocoulometry was adapted for this measurement. This method allows quantitative determination of single- and double-stranded DNA with a detection limit of 10^{11} DNA molecules/cm^2. Together these studies demonstrate that the protocol for attachment of DNA-functionalized SAMs that we have developed achieves at least 60 % theoretical coverage with essentially 100 % activity of the surface immobilized DNA.

Awards in FY98:

Mr. John Houser was awarded the Department of Commerce Bronze Medal for outstanding contributions to the development of primary standards for liquid volume and density measurements, for provision of calibration services of the highest quality, and for exceptional support to customers. Dr. Rastislav Levicky received the Sigma Xi award for best postdoctoral poster at this year's Post Doctoral Poster Presentation. His work was titled: "Using Self-Assembly to Control the Structure of Surface-Tethered DNA". **Dr. Steve Semancik** was named as Fellow of the American Vacuum Society for his outstanding contributions to the understanding of the chemical and electronic properties of oxides and catalytic metals. **Dr. George Mattingly** received the Lewis M. Moody award from the American Society of Mechanical Engineers (ASME) for his paper "Flow Measurement Proficiency Testing for International Comparison and Traceability". This award is given for the paper of "most practical value to mechanical engineering" presented at the Annual Meeting of the ASME.

Drs. Archie Miiller and Charles Tilford received the NIST Measurement Services Award in the calibration category for their outstanding efforts in extending the range of NIST's primary calibrations of vacuum by an order of magnitude via high accuracy manometry.

Organizational Structure:

In FY98 the Division organization was stable with six Groups: Fluid Flow, High Temperature Processes, Reacting Flows, Process Sensing, Thermometry, and Pressure and Vacuum. The following pages present more detailed discussions of some of the accomplishments and plans for the coming year for many of the Division's programs.

B. Selected Technical Reports

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

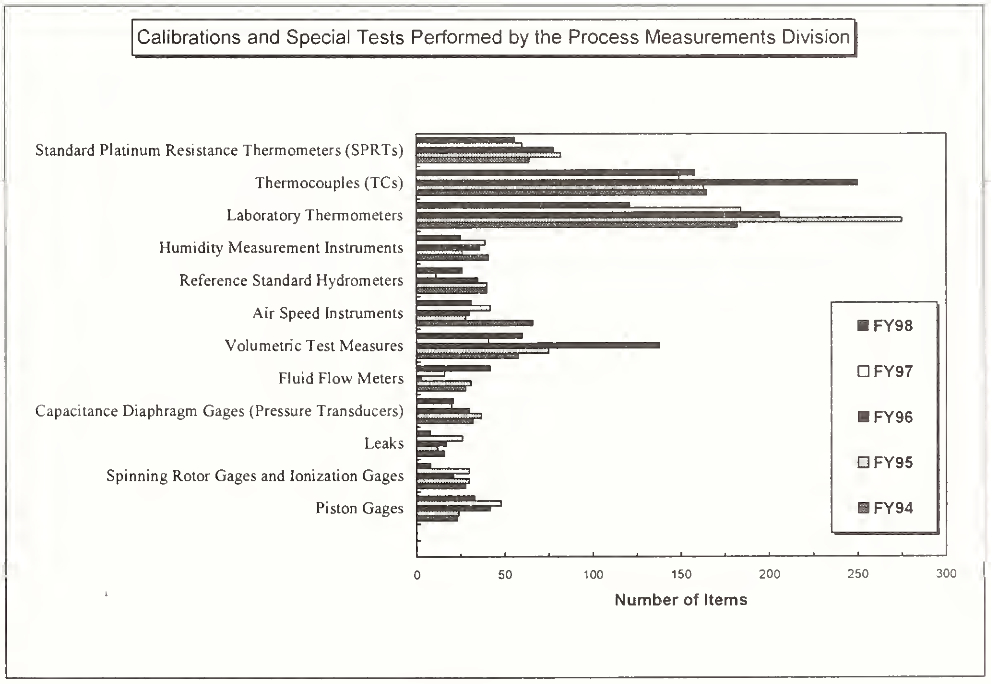
G.J. ***Rosasco****, V.E. Bean, B.W. Mangum, G.E. Mattingly, and S.A. Tison*

Objective: To realize and maintain national standards according to the definitions of the relevant units, and to disseminate the NIST-realized units to industry and government agencies (federal and state governments) that require calibrations against and direct traceability to national standards.

Problem: The Process Measurements Division is responsible for realizing, maintaining, and disseminating the national standards for measurement of temperature (in the range 0.65 K to 1235 K), pressure, vacuum, gaseous leak rate, humidity, fluid flow rate, liquid volume and density, and air speed. Issues of primary importance in this area involve assessing and meeting, to the extent practicable, customer requirements in terms of types and ranges of service and levels of uncertainty, improving the efficiency of calibration services, developing methods to enable appropriate realization of standards in the customer's laboratories, and serving as the primary resource supporting the national measurement system.

Approach: Provision of customer-appropriate access to national standards of measurement involves a range of activities: maintenance and improvement of primary standards, participation and leadership in U.S. and international standards activities, performance of instrument calibrations and tests, operation of Measurement Assurance Programs, proficiency and round-robin tests, development of mechanisms for realization of secondary standards in customer laboratories, and a wide-range of consultation and customer assistance services. The calibration and test services provided by the Division are described in NIST SP250, NIST Calibration Services Users Guide, and its supplements.

Results and Future Plans: The chart below summarizes the level of activity in each service area over the past five years. Large fluctuations in numbers of items are often encountered, however the total calibration workload typically varies by less than 20 %. Our capabilities, experimental techniques and the facilities used to provide these services are continually upgraded, with concomitant improvements in efficiency and in measurement uncertainties. Improvements of standards and highlights of activities for temperature, humidity, low-range gas flows, and liquid density are discussed in separate reports below. Also presented in separate



reports are descriptions of our extensive involvement in international comparisons, a critical element in maintaining the position of the Nation's measurement system in the world.

As part of an EPA program designed to assess the accuracy of reference methods for measuring the volumetric flow in smoke stacks, the Fluid Flow Group calibrated 33 Pitot static probes used by EPA in field tests. To meet EPA's needs, the NIST facility and procedures were modified to include the measurement of yaw angle, sensor response as a function of pitch angle, and the redundancy of using three differential pressure measurement systems with the seven types of probes. EPA is currently assessing the impact these data and data from other sources will have on their test method.

The Division commissioned a new gravimetric volume calibration facility in FY95. This capability, developed in collaboration with the American Petroleum Institute, has raised the NIST primary standards for volume to the state-of-the-art both nationally and internationally. This year the Fluid Flow Group completed its first participation in an international comparison of liquid volume standards. Collaborating with Mexico (CENAM) and Germany (PTB), who also have gravimetric standards, we compared calibrations of a 50 L test measure. The results from the three laboratories agreed within their stated uncertainties. The NIST value deviated by less than 10 ppm from the average and had the smallest expanded relative uncertainty of 17 ppm ($k = 2$).

The interest in developing advanced flow measurement technology for variable temperature and variable composition gas flows, for example, for measurements on vehicle exhausts, continued this year with six flow-meters tested in the recently commissioned Heated Mixture Gas Flow Facility. This testing has characterized the behavior of ultrasonic, vortex shedding, laminar, and dilution flowmetering devices in direct collaborations with the industrial developers of the meters.

In FY98 we continued to upgrade our water flow measurement standards. These efforts have extended those made previously in our 250 mm-dia pipe-work to our 200 mm line. Enhanced flow conditioning elements have been designed and implemented in accord with our Computational Fluid Dynamic (CFD) modeling capabilities. Additionally, we have added a scaled version of the ultrasonic flowmetering unit used in our 250 mm-dia line. This is a multi-path, in-line, travel-time device that not only provides real time flow measurements, but also monitors the pipe flow profiles entering the meter being tested. Pipe flow profile measurements using laser Doppler velocimetry (LDV) also have been done to confirm that the enhanced flow conditioning is achieved and that the diagnostics from the ultrasonic meter are satisfactory. These enhancements will enable us to make a unique contribution to an international flow-standards comparison. This comparison, initiated at the National Engineering Laboratory (NEL) in the UK, has produced testing in the NMIs of The Netherlands and Japan. The program uses a 200 mm-dia tandem orifice metering transfer standard. As a result of our efforts, NIST will be the only laboratory with direct characterization of the flow conditions entering the transfer standards and simultaneous use of an ultrasonic meter to provide another (primary) measurement of the flow. We hope to evolve this program into a worldwide one that quantifies the degree of equivalency of the standards in the participant labs in Europe (EUROMET) and Asia (APMP), and North America (NORAMET). To this end, we have arranged for tests to be done in Mexico (CENAM) and at the Alden Research Laboratory (ARL) in Massachusetts so that an appropriate NORAMET representation is generated for the program; Canada does not yet have a laboratory with the required facilities to join this program.

The Division made significant progress in producing the required documentation that supports our compliance with ANSI/NCSL Z540-I-1994. This is the U.S. standard, specific to calibration laboratories, defining the requirements for the ISO 9000 series of standards and ISO/IEC Guide 25 as they apply to calibration laboratories. The documentation is contained in the Division Quality Manual. Part I, which applies generically to all services provided by the Division, is complete, and Part II, which deals with the specifics of each service, has been completed for most services. These efforts will continue in FY99.

Publications:

Tew, W.L., Strouse, G.F., and Meyer, C.W. ***"A Revised Assessment of Calibration Uncertainties for Capsule Type Standard Platinum and Rhodium-Iron Resistance Thermometers,"*** NISTIR 6138 (1998).

Tilford, C.R., Miiller, A.P., and Shillang Lu, ***"A New Low-Range Absolute Pressure Standard,"*** Proceedings of the 1998 National Conference of Standard Laboratories, 245 (1998)

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

B. W. Mangum, *C. W. Meyer, W. L. Tew, G. F. Strouse, D. C. Ripple, G. W. Burns, K. M. Garrity, C. D. Vaughn, G. T. Furukawa (Guest Researcher), W.C. Ausherman, E. Y. Xu (Geocenters) and N. P. Moiseeva (VNIIM, D. I. Mendeleyev Research Institute of Metrology, St. Petersburg, Russia)*

Objective: To realize and maintain the International Temperature Scale of 1990 (ITS-90) as it is defined over the range from 0.65 K to 1235 K, to investigate the non-uniqueness of the ITS-90 over this temperature range, and to disseminate the scale to the user community.

Problem: The ITS-90 extends upward from 0.65 K. The realization of this scale, as it is defined, has been completed at NIST over the ranges from 0.65 K to 1234.93 K, as reported in "Guidelines for Realizing the International Temperature Scale of 1990 (ITS-90)," *NIST Technical Note 1265*, U.S. Govt. Printing Office, Washington, DC 20402, August 1990, and in several papers published in: *Temperature: Its Measurement and Control in Science and Industry*, Vol. 6 (Edited by J. F. Schooley), New York, American Institute of Physics, 1992; *Metrologia*; *Proceedings of TEMPMEKO '96, 6th International Symposium on Temperature and Thermal Measurements in Industry and Science*, (Edited by P. Marcarino), Torino, Levrotto & Bella, 1997; and *International Seminar on Low Temperature Thermometry and Dynamic Temperature Measurement*, 1997. Sealed triple-point cells of Ar, O_2, Ne, and equilibrium H_2 are needed for maintaining the realization of the scale in the cryogenic region, and for participating in international comparisons of realizations of the scale defined by these fixed points. Although our realization of the ITS-90 has reduced the uncertainties in our calibrations, there still are uncertainties resulting from the non-uniqueness of the scale over the range from 13.8033 K to 1243.93 K that must be determined in order to arrive at the total uncertainties in realization and in calibrations. Also, better methods for dissemination of the ITS-90 are needed to get the scale to users requiring high accuracy.

Approach: The completion of the implementation of the ITS-90 will be accomplished through the realizations of the triple-point temperatures of Ar (83.8058 K), O_2 (54.3584 K), Ne (24.5561 K) and e-H_2 (13.8033 K) in transportable cells that are required for maintaining the scale over this range of temperatures and that also are suitable for use in international comparisons. The non-uniqueness of the ITS-90 will be determined by investigating its sources in the various temperature ranges from 13.8033 K to 1234.93 K and determining its magnitude in the different ranges. Since many thermometers are required for this investigation, collaborations with national laboratories of other countries are desirable, or necessary, in order to have enough thermometers for a meaningful investigation of the range from 933 K to 1235 K. The ITS-90 is disseminated through calibrations of thermometers, SRM fixed-point cells of pure materials, SRMs of pure metals of the defining fixed-point materials, and SRM thermometers.

Results and Future Plans: We performed additional realizations of the defining triple points of the ITS-90 from 13.8033 K to 83.8058 K in order to retain the scale on additional standard platinum resistance thermometers (SPRTs) and rhodium-iron resistance thermometers (RIRTs), some of which will be used in international comparisons as described in Section 5.

Triple points of O_2 and Ar in sealed cells were investigated in FY98 and found to be extremely stable over long times. Cells of Ne were investigated also, but since there appeared to be some impurity present, more work is required, using cells filled from different sources of Ne. Sealed transportable cells of e-H_2 and Hg also will be constructed and evaluated in FY99. The international comparison of our triple-point cells of e-H_2, Ne, O_2, Ar, and Hg in FY99 is described in Section 5.

Although we have realized the ITS-90 from 0.65 K to 1234.93 K, the determination of the non-uniqueness in the range from 13.8033 K to 24.5561 K, arising from the use of SPRTs and an interpolating, constant-volume gas thermometer, and that at higher temperatures, resulting from use of SPRTs, has not been completed. Efforts to determine the non-uniqueness in the ranges 273.16 K to 933.473 K and 933.473 K to 1234.93 K, however, were continued this year. Since our supply of high temperature SPRTs is inadequate for the range 933 K to 1235 K, we organized previously a collaborative effort with the national laboratories of Italy (IMGC) and the Netherlands (NMi/VSL). Comparison measurements on seven of the NIST HTSPRTs that had been selected for investigation on the basis of their stability upon high-temperature exposure and that had been calibrated from 273.16 K to 1234.93 K were continued in the range from 933 K to 1235 K in our high-temperature comparator. All measurements obtained to date on the seven HTSPRTs indicate a non-uniqueness (less than 2 mK) that is significantly smaller than that observed at IMGC for their first set of HTSPRTs. During FY99, the investigation of all of NIST's HTSPRTs is expected to be completed and study of IMGC's HTSPRTs will begin. The investigation of non-uniqueness in the range 13.8033 K to 24.5561 K is expected to be completed in FY99.

In recent years, we have had a significant effort in certifying fixed-point cells, thermometers, and high-purity metals (for use in fixed-point cells), with the goal of disseminating the ITS-90, or of providing materials for use in its realization, to secondary calibration laboratories and others requiring high accuracy. In this effort, work on the certification of 99.9999+ % pure Sn for SRM 741a [Sn (freezing-point)] began in FY97 as a replacement for SRM 741 and it was completed in FY98. Work on SRM 1751, the [(Ga (melting-point)] began in the last quarter of FY98 and will be completed in FY99. Work on another new SRM of calibrated capsule SPRTs, covering the range from 13.8033 K to 429.7485 K, began in FY97, continued in FY98, and will be completed in FY99. Also, dissemination of the ITS-90 to those requiring high accuracy
(± 0.01 K) at temperatures up to 1273 K is provided by highly stable and accurate thermocouples (TCs) that require no recalibration. In this regard, the certification process of 18 Au/Pt TCs (SRM 1749) was completed in FY98.

Publications:

Strouse, G.F., "***Standard Reference Material 1745: Indium Freezing-Point Standard and Standard Reference Material 2232: Indium DSC Melting-Point Standard,***" NIST SP 260-132, 1998.

Tew, W.L. and Strouse, G.F., "***The Capsule-Type Standard Platinum Resistance Thermometer as a Standard Reference Material: SRM 1750,***" Proc. 1998 National Conference of Standards Laboratories, 1998.

Tew, W.L., Meyer, C.W., Strouse, G.F., and Furukawa, G.T., "***Recent Advances in the Realization and Dissemination of the ITS-90 Below 83.8 K at the National Institute of Standards and Technology,***" Advances in Cryogenic Engineering, 43, 733-740, Plenum Press, New York, NY (1998).

Strouse, G.F. and Moiseeva, N.P., "***Standard Reference Material 741a: Tin Freezing-Point,***" NIST SP 260-138, 1998.

3. *High-Temperature Thermocouple Research and Surface Temperature Measurements*

***D. C. Ripple**, G. W. Burns, K. G. Kreider, C. W. Meyer, B. W. Mangum, D. P. DeWitt (Optical Technology Division), D. W. Allen (Geocenters) and M. Battuello (IMGC)*

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

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

Approach: To address the need for stable TCs, as indicated in (1) above, TCs of pure noble metals, such as Au, Pt, and Pd, are being investigated. These metals can be produced at very high purity (5 to 6 nines, depending on the metal) and are generally resistant to oxidation in high-temperature environments. Since the TCs are constructed of these pure metals, inhomogeneities are small, defects can be removed by annealing, and the TCs are stable and, in the case of Au/Pt, interchangeability is excellent. To address the need for accurate measurements of temperatures of surfaces, the feasibility of thin-film TCs is being investigated. These devices become part and parcel of the surface and thereby obviate the uncertainties associated with conventional contact thermometers (uncertainty of the quantitative relationship of the measured temperature and the surface temperature) and with radiation thermometers (uncertainty with respect to the time-dependent, effective emissivity of the surface, stray radiation, and changes in the optical path).

Results and Future Plans: In our efforts to develop stable, high-accuracy TCs, we found previously that Au/Pt TCs are an excellent choice for temperatures up to 1275 K (stability of a few mK) and we developed a reference function for them. The certification process for Au/Pt TCs as SRM 1749 was completed in FY98. A paper on Au/Pt TCs will be written in FY99. A collaborative project with Istituto di Metrologia "G Colonnetti" - Torino (IMGC) investigating Pt/Pd TCs for use to about 1775 K was completed in FY98. These TCs also have been found to be excellent thermometers, with stabilities of 5 mk to 10 mK per 100 h at 1375 K and inhomogeneities equivalent to only 4 mk to 16 mK. In order to confirm that the TC measurements performed at IMGC against a radiation thermometer at temperatures up to 1775 K do not have a large systematic error, calibrated Pt/Pd and type S TCs were compared in the range 973 K to 1775 K at NIST. Differences in indicated temperatures of those TCs were < 0.1 K up to 1375 K and < 0.4 K from 1375 K to 1775 K, well within the combined uncertainties of calibrations of the two TCs. We found also that changes in thermoelectric properties of Pt/Pd TCs heated to 1775 K had some reversible and some irreversible components. We completed the analysis of all of the data on the Pt/Pd TCs up to 1775 K and developed a reference function for them. Comparison of the NIST/IMGC reference function with previously published data on Pt/Pd TCs revealed large discrepancies at temperatures > 1470 K. To demonstrate that these discrepancies were not caused by the different purity Pd wires used in the different studies, the emf differences from 923 K to 1775 K between a Pt/Pd TC included in the NIST/IMGC study and a set of TCs fabricated with lower purity Pd wires were measured. The results demonstrated that with proper techniques, the calibration of Pt/Pd TCs with moderate purity Pd wire may be reliably extrapolated to 1775 K. A paper on Pt/Pd TCs was written in FY98 and it was accepted for publication by *Metrologia*. The paper incorporated extensive statistical calculations on the uncertainty of the reference function. Industrial trials of Pt/Pd TCs in diffusion furnaces used by the semiconductor industry were started in FY98, but results have not yet been obtained from the company involved.

We continued the investigation of using thin-film TCs with high-spatial resolution (< 1 mm) and short response times (ms) to improve the accuracy of surface temperature measurements in the semiconductor manufacturing industry (especially for RTP). An improved method for determining the Seebeck coefficient of the thin-film TCs on silicon wafers was developed this year. Using a finite-element analysis model of the heat transfer in the test, the uncertainty ($k=1$) of the measured Seebeck coefficient is estimated to be 3 %, corresponding to an uncertainty of < 2 K in the measured surface temperature of the wafer when those measurements are combined with those of the Pt/Pd wire TCs attached to the periphery of the wafer. This improved calibration of the thin-film TCs should lead to a significant improvement in the *in-situ* calibration of radiometers used in RTP tools. Using the NIST RTP test bed, we have tested some Pt/Pd and Rh/Pt thin-film TCs on silicon wafers, combined with Pt/Pd wire TCs attached to the periphery of the wafers. The Pt and Pd films are stable up to 1100 K in the RTP environment and the Rh films are stable up to 1200 K. Pt and Pd wires of 0.1 mm and 0.25 mm diameter were used in constructing the wire TCs to measure the temperature of the wafers at their periphery and also to serve as leads to the thin-film TCs. After thin-film TCs were deposited on test wafers, SensArray, Inc., Santa Clara, CA, instrumented those wafers with small-wire base-metal TCs. Radiation thermometers and these different types of TCs on the wafers then were used in making preliminary measurements of temperature of the wafer surface in the RTP tool at various temperatures. During FY98 the RTP tool was redesigned to better model the radiation environment and reduce the uncertainties of the radiation measurements. Three papers on our work were presented to the RTP and Instrumentation Society communities. In FY99, Ir and Ru thin-film TC-instrumented wafers will be investigated for durability, stability and repeatability in simulated industrial RTP environments at temperatures up to 1300 K; TC-instrumented wafers will be used for *in-situ* calibration of radiometers; and measurements with those radiometers will be compared with those calibrated in blackbodies.

Publications:

Burns, G.W., Ripple, D.C., and Battuello, M., "***Platinum Versus Palladium Thermocouples: an emf-Temperature Reference Tunction for the Range 0°C to 1500 C,***" Metrologia, in press.

Battuello, M., Burns, G., and Ripple, D., "***Measurements Towards an ITS-90 Based Reference Function for Pt/Pd Thermocouples from 0 °C to 1500 °C,***" EUROMET Workshop on Pt/Pd Thermocouple Behaviour, Paris, 1998.

Kreider, K.G., DeWitt, D.P., Tsai, B.K, Lovas, F.J, and Allen, D.W, "***RTP Calibration Wafer Using Thin-Film Thermocouples,***" Rapid thermal and integrated processing VII, M. Ozturk, Ed., Materials Research Society, Pittsburgh, PA, 1998, 525 . 87-94.

Kreider, K.G., Ripple, D.C., and DeWitt, D.P., "***Determination of the Seebeck Coefficient of Thin-film Thermocouples,***" Proc. 44th International Instrumentation Symposium, May 3-7, 1998, Reno, NV, 561-570.

4. *Thermodynamic Temperature Measurements*

D. C. Ripple*, B. W. Mangum, D. DeFibaugh (Division 838), M. Geide (Division 838), and M. Moldover (Division 838)*

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

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

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

Results and Future Plans: In FY98 efforts focused on fabrication of the acoustic resonator and the associated transducers, pressure vessel, and furnace. Electrical, mechanical, and acoustic properties of the acoustic transducers (capacitance diaphragm-type using very thin discs of pure Si) built for the resonator were measured. Modifications were made to the transducers to improve their mechanical durability and to improve their acoustic sensitivity. Construction and assembly of the high-stability furnace continued. To reduce heat leaks, and corresponding thermal gradients between the pressure can and the resonator, the furnace design was modified. Automation of the measuring system progressed well, with completion of conversion of old software from Division 838, and the near completion of software for data acquisition and least-squares fitting of both acoustic and microwave signals. The testing of automated control of the gas handling system is in progress.

During the first months of FY99, the resonator and the inner furnace stage will be fully assembled. The microwave and acoustic properties of the resonator will be measured near room temperature. After these initial tests, the resonator will be operated at increasingly higher temperatures and the effects of baking and resonator purging on the argon purity will be studied.

5. *International Comparisons of Temperature Standards and Scale Realizations*

***B. W. Mangum**, G. F. Strouse, W. L. Tew, C. W. Meyer, and G.T. Furukawa*

Objective: To serve as coordinator for, and/or participate in, comparisons of national realizations of the International Temperature Scale of 1990 (ITS-90) and of some transportable cells of the defining fixed points of the scale.

Problem: There have been some bilateral as well as some multi-national comparisons of fixed-point cells of some defining fixed points, however, there have been no general comparisons of realizations of the ITS-90 or of the defining fixed points over the entire range of the scale at the highest levels of accuracy. Results of such comparisons are needed in order to develop a basis for bilateral agreements between the U.S. and other countries on the realizations of the kelvin (through the ITS-90) and of the other SI units. Such agreements are necessary for trade purposes.

Approach: We will participate in four key comparisons of realizations of the ITS-90 organized by the CCT, and in a comparison of transportable cryogenic triple-point cells organized by PTB. NIST is coordinating key comparison 3 covering the range from 83.8058 K (Ar triple point) to 933.473 K (Al freezing point), with 14 national laboratories plus BIPM participating. NML and PTB are serving as our sub-coordinators for some of the laboratories. Also, NIST is serving as sub-coordinator for comparison 4 covering the range from 933.473 K to 1234.93 K (Ag freezing point). Both sets of comparisons involve circulating some fixed-point cells and an HTSPRT. After measurements are completed by each of the participants, the devices are returned to NIST or the appropriate sub-coordinator for another set of measurements before they are sent to the next participant. We are participating also in key comparison 1 of realizations of the ITS-90 over the range 0.65 K to 24.5561 K, involving RIRTs, and key comparison 2 of realizations over the range 13.8033 K to 273.16 K, involving capsule SPRTs (CSPRTs). It is the intention to expand key comparisons 3 and 4 to CENAM as part of a NORAMET project, with NIST serving as coordinator. Also, we will participate in a SIM project on comparisons of calibrations of various types of thermometers.

Results and Future Plans: Key comparison 3 covering the range from 83.8058 K to 933.473 K was initiated in FY97 and continued in FY98. The schedule for the measurements by the various participants was altered due to unexpected complications. Additional sets of Ga and Cd fixed-point cells used in the comparisons were prepared and evaluated. Also, additional SPRTs used in the comparisons were evaluated for stability and measured at all of the defining fixed points in the range, and at the Cd freezing point. After measurements at NIST and by the sub-coordinator, NML or PTB, the devices were sent by NML and PTB to their respective participants. In Asia, coordinated by NML, measurements have been completed at MSL/IRL (New Zealand), NRLM (Japan) and KRISS (Korea), with intermediate measurements at NML, and the devices are now at NIM (China). In Europe, coordinated by PTB, measurements have been completed at VNIIM (Russia), INM (France) and SMU (Slovakia), with intermediate measurements at PTB, and the devices are now at NPL (UK). Additionally, we sent a set of devices to NMi/VSL (Netherlands) and to NRC (Canada) for measurements, with intermediate measurements at NIST, and the devices are now at IMGC (Italy). Results have been received from only four laboratories. After all measurements have been completed in Asia and Europe during the first quarter of FY99, the devices will be returned to NIST for the final set of measurements. After those measurements, the data from all the participants will be analyzed at NIST and a report prepared for submission to the CCT at its next meeting in June 1999.

Key comparison 4, covering the range from 933.473 K to 1234.93 K and for which NIST (sub-coordinator for PTB) is responsible for the participants NRC and IMGC, began in FY98 and will be completed in FY99. Al and Ag freezing-point cells from PTB were brought to NIST for comparison with NIST's cells to start the sequence of comparisons. After NRC compared their and our cells, using our HTSPRTs, our devices were returned to us for intermediate measurements before they were delivered to IMGC. The devices will be returned to NIST by December 1998 for the final set of measurements at NIST. The results from NIST, PTB, NRC, and IMGC will be analyzed and reported to

PTB for inclusion in a report to the CCT for its June 1999 meeting.

In addition to serving as coordinator for CCT key comparison 3 and sub-coordinator for key comparison 4, NIST is participating in key comparison 2 (13.8033 K to 273.16 K) by providing to NRC (coordinator) two CSPRTs that were accurately compared with other NIST CSPRTs on which the NIST realization of the ITS-90 is retained. Also, we delivered two of the RIRTs on which our realization of the ITS-90 from 0.65 K to 24.5561 K is retained to NPL (coordinator) for participation in key comparison 1. Key comparisons 1 and 2 will be completed in FY99 and the NIST CSPRTs and RIRTs returned to NIST for follow-up measurements.

Several O_2, Ar and Ne triple-point cells were evaluated for selection of one of each to be sent to PTB to be used in the comparison of sealed, cryogenic-triple-point cells being organized by PTB for a EUROMET project. An O_2 and an Ar cell were selected. Since the Ne sample appeared to contain an impurity, more work on cells of Ne from different sources are required in FY99 before selecting a Ne cell to send to PTB. Equilibrium H_2 and Hg triple-point cells will be constructed in FY99 and evaluated in order to select one of each to send to PTB for inclusion in the comparison. Since the NIST O_2 cell contains pure O_2 prepared from decomposition of $KMnO_4$, its comparison with those of the European laboratories that use commercially-available pure O_2 as their source will be extremely interesting and important.

We will begin the NORAMET and SIM projects in FY99, with NIST providing the relevant fixed-point cells and (HT)SPRTs to CENAM for the NORAMET project and thermocouples for the SIM project.

6. *Standards for Measuring Low Flow Rates of Gases*

***R.F. Berg**, A.M. Calabrese, and S.A. Tison*

Objective: To develop primary flow standards in the range from 10^{-7} mol/s to 10^{-3} mol/s and to transfer this flow measurement capability to U.S. industry, government, and academic institutions.

Problem: Many industrial processes require the accurate metering of mass flow rate over the range from 10^{-7} mol/s to 10^{-3} mol/s. In particular, the SEMI/SEMATECH Mass Flow Controller working group identified the need to measure flow rates in this range with uncertainties of 1 % or less and identified the need for national flow standards with uncertainties of 0.2 % or less. To meet these needs, new primary flow standards and improved flow measurement techniques for industrial applications must be developed.

Approach: We have implemented a program to develop primary flow standards that would operate over a range from 10^{-7} mol/s to 10^{-3} mol/s with uncertainties of 0.1 % or less. To transfer this measurement capability to industrial users, the properties of commercially available flowmeters have been investigated, and the development of highly repeatable secondary flow standards, especially those showing promise for corrosive gases, will be continued.

Results and Future Plans: In an effort to further reduce uncertainties over the existing primary flow standard from 10^{-7} mol/s to 10^{-3} mol/s, a constant-pressure flowmeter has been constructed. This flowmeter uses optical interferometry to measure and control the displacement of a piston of known cross-section. Controlling the piston's rate of displacement maintains a constant pressure in the gas accumulation volume, which significantly reduces one source of measurement error. This new candidate for a primary standard will be tested and compared with the existing primary standard, a constant-volume flowmeter. It will ultimately replace the constant-volume standard and be used for characterization of laminar flowmeters, acoustic flowmeters, and other secondary and transfer flow standards.

During the past two years, a prototype acoustic flowmeter has been constructed and characterized. This device measures the sound speed through a stagnant test gas, as well as the phase shift of sound propagation through the flowing test gas. Knowledge of the sound speed through a duct of known cross-sectional area, obtained from *in-situ* measurements, allows conversion of the flow-induced phase shift to a flow velocity, and thus a volumetric flow rate. The gas's equation of state (nearly ideal) plus measurements of pressure and temperature allow conversion to a mass flow rate. This approach has great advantages over current flowmeters, which depend upon knowledge of local gas properties such as heat capacity or viscosity. The acoustic flowmeter's present resolution is approximately 0.05 % of the full scale flow of 10^{-3} mol/s, but its uncertainties are unacceptable. Planned measurements will test recently developed theories of sound propagation in ducts with flow in an effort to reduce the flowmeter's uncertainties.

NIST recently developed secondary flow standards based on maintaining laminar flow through a thermostatted helical channel, where gas viscosity is the only gas-specific variable. Tests at NIST have established the utility of this standard where the viscosity-adjusted flow rates of five gases were correlated to within 0.2 %. During the last year, we also used these devices as transfer standards to conduct proficiency tests of primary and secondary flow standards at four industrial sites Further refinements and uses of these secondary standards is planned.

Publications:

Tison, S.A., ***"Flow Metrology Support and Digital MFCs,"*** Solid State Tech. 41, 73 (August 1998).

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7. *Comparison of International Pressure Standards*

A.P. Miiller, *J.P. Looney, J.W. Schmidt, C.R., Tilford, and S.A. Tison*

Objective: Establish functional agreement between national pressure and vacuum standards for pressures between 3 x 10^{-7} Pa and 500 MPa.

Problem: International trade is, in part, based upon the equivalence of measurements. Some of the largest segments of industrial measurements are in the areas of pressure and vacuum. To help alleviate technical trade barriers, the relative agreement of national measurements standards needs to be assessed, established, formally recognized, and maintained.

Approach: The sixth meeting (May 29-30, 1996) of the Consultative Committee for Mass and Related Quantities (CCM) identified six Key international comparisons in pressure and vacuum measurements, their ranges, the transfer standards to be used, and the National Measurement Laboratory (NML) that would act as the pilot laboratory:

Results and Future Plans: The Low and Medium Pressure Working Group of the CCM has organized a comparison of vacuum pressure standards, Line 1, Table 1, for which NIST has agreed to serve as pilot laboratory. This comparison will be carried out between NIST, the National Physical Laboratory - Teddington (NPL - UK), the Istituto di Metrologia "G Colonnetti"-Torino (IMGC), the Physikalisch-Technische Bundesanstalt-Braunschweig (PTB), the Korean Institute of Standards and Science (KRISS), and the National Physical Laboratory – New Delhi (NPL-India). Other laboratories expressing interest in the inter-comparison include the Laboratoire National D'Essais -Paris (LNE), and the National Research Laboratory for Metrology – Tskuba (NRLM), pending the qualification of their new standards. A transfer standards package has been

Table 1

Pressure Range	Transfer Standard	Pilot Lab
$3x10^{-7}$ Pa to $1x10^{-3}$ Pa (absolute)	Spinning Rotor & Ion Gauges	NIST
1 Pa to 1 kPa (absolute)	Low pressure transducers	NIST
1 Pa to 1 kPa (differential)	Low pressure transducers	NIST
10 kPa to 120 kPa (absolute)	Pneumatic piston gauge	NPL - UK
50 kPa to 7 MPa (gauge)	Pneumatic piston gauge	LNE
50 MPa to 500 MPa (gauge)	Hydraulic piston gauge	NRLM

developed at NIST that consists of two spinning rotor gauges, and two types of ion gauges (glass Bayard-Alpert gauges and a variation of this gauge known as a Stable-Ion gauge). We have completed the initial calibrations of the transfer standard package and the protocols are currently under discussion. The initial phase of this comparison will begin in early 1999.

Two comparisons of standards operating in the pressure range 1 Pa to 1 kPa, Lines 2 and 3, Table 1, have been organized by the Low-and-Medium Pressure Working Group of the CCM for which NIST has also agreed to serve as pilot laboratory. The absolute pressure comparison will involve seven laboratories: NIST, PTB - Berlin, NPL - UK, IMGC, CSIRO-NML (Australia), KRISS, and NPL - India. The differential pressure comparison will involve five laboratories: NIST, CSIRO, NPL - UK, IMGC, and MSL - New Zealand. NIST developed a transfer standard that includes four differential pressure transducers (two capacitance diaphragm gauges and two resonant silicon gauges) and an integral ion vacuum pump to establish the necessary reference vacuum for absolute pressure comparisons. The same package can also be used for differential pressure comparisons, with the ion pump turned off. The protocol for each comparison has been finalized after taking into account comments from the participants on earlier draft versions. In order to ensure a timely completion of these comparisons, two identical transfer standards packages (A and B) were constructed and calibrated at NIST. Transfer Package A is currently being circulated through the European region, and Package B through the Asia Pacific region with a target completion date for the experimental work of June 1999.

The results of an earlier comparison (Line 4, Table 1) demonstrated significant differences between some national standards. As a result, this comparison has been extended to a second phase and will use a new transfer standard. This phase has just gotten underway and will involve NPL-UK (pilot laboratory), NIST, Bureau International des Poids et Measures (BIPM), Insitut National de Metrologie (INM-France), CSIRO, PTB - Braunschweig, IMGC, National Research Council (NRC-Canada), NMi (Netherlands), OFMET (Switzerland), INM (China), and VNIIMS (Russia).

A comparison of intermediate gas pressure standards, Line 5, Table 1, has been organized by the High-Pressure Working Group of the CCM. The LNE agreed to serve as pilot laboratory for a first phase. This phase, between 50 kPa and 1 MPa, has been carried out between five laboratories: NIST, NPL - UK, IMGC, PTB - Braunschweig, and LNE. The data for phase one are complete and are now being analyzed as phase two is being implemented. Phase two is a comparison over the range of 500 kPa to 7 MPa and includes the laboratories in phase one with the addition of the NRLM.

A comparison of high pressure standards (50 MPa to 500 MPa) in hydraulic media, Table 1, has also been organized by the High-Pressure Working Group of the CCM. The NRLM has agreed to serve as the pilot laboratory. This comparison has recently begun among the four NMLs: NRLM, NIST, NPL - India, and KRISS.

8. *Development of Quantitative Measurements for Vacuum Process Control*

C.R. Tilford, T. Gougousi (Univ. Maryland), and S.A. Tison

Objective: Support semiconductor process-control development with improved residual gas or partial pressure analyzers (RGAs or PPAs), and *in-situ* RGA and gas flow calibration techniques.

Problem: The increasing volume and complexity of vacuum processing, most notably in the semiconductor industry, requires improved real-time process monitoring and control of process gases, reaction products, and gaseous contaminants. Residual gas analyzers are the most promising candidates for this task, and are already used in a variety of vacuum processes, but their often unpredictable performance has limited these applications. Realizing their potential requires a better understanding of the factors limiting their performance, and the development of *in-situ* calibration techniques for highly reactive process gases. In addition, gas flow rate has been established as one of the principal control parameters in semiconductor processing, however, there is a further need to calibrate the process instruments, Thermal Mass Flow Controllers (TMFCs), with reactive process gases.

Approach: Obtain quantitative test data for commercial RGAs and develop generic RGA operation models that will allow a determination of critical performance parameters, optimum operational conditions, and instrument design improvements. Transfer NIST vacuum standards capabilities to users through the development of *in-situ* process-gas calibration techniques for both RGAs and TMFCs. Collaborate with the University of Maryland (UMD) in testing these calibration techniques and applying calibrated instruments to the control of a tungsten deposition process.

Results and Future Plans: Experimental RGA performance characterization and analytic modeling carried out by NIST in previous years show that the performance of RGAs is strongly influenced by electron and ion space charge in different parts of the instruments. For many RGAs this understanding allows adjustment of the instruments to minimize the most serious defects—severe non-linearities with pressure and a correlated dependence of the sensitivity for one species on the pressures of other species. These studies were carried out with conventional open-ion-source RGAs, but during the past year they have been extended to the newer closed-ion-source (CIS) RGAs, which are specifically designed to work with reactive process gases. For this phase of the experiment two different CIS-RGAs, and two conventional RGAs from the same manufacturers and of the same designs except for the ions sources, are being tested with inert gases using the NIST RGA calibration apparatus. We expect that parallel testing of the two types of RGAs will indicate how much of our experience with open-source RGAs is applicable to the CIS instruments. It is expected that this phase of the experiment will continue for another three to six months, but for at least one pair of instruments, initial results indicate that the non-linearities in the conventional RGA are significantly larger than those observed for its CIS mate, which is consistent with our understanding of space charge effects. The other pair of instruments both exhibit relatively small non-linearities.

During this past year we initiated an active collaboration with a University of Maryland group that is investigating the control of a tungsten deposition process, using a commercial semiconductor process tool and RGAs as process sensors. This has already proven mutually beneficial; NIST has considerably broadened its experience to include the problems associated with two notoriously reactive gases, WF_6 and HF, and the quirks of commercial process tools. At the same time, NIST RGA experience has helped in the understanding of initial experimental results. These results, obtained with UMD RGAs, exhibit a definite correlation between process parameters and RGA measurements, but do not yet show the quantitative correlation required for process control. Currently, changes are being made in the RGA sampling system, and upon completion of the inert-gas testing at NIST, we plan to install one of the NIST CIS-RGAs on the UMD tool. Both the NIST and UMD RGAs will be calibrated with WF_6 using a process-gas *in-situ* calibration system to be developed by NIST.

The UMD tool includes 12 TMFCs, and these were a source of problems during the start-up phase.

NIST-calibrated TMFCs were used to find defects in the TMFCs and their control system. After system repairs the TMFCs were calibrated by NIST with nitrogen (the industry practice), but a quantitative understanding of the control process requires calibration with WF_6, a capability that does not yet exist at NIST, or elsewhere to the best of our knowledge. NIST has built a portable rate-of-rise flow standard, designed to minimize decomposition of WF_6. This will be tested in the coming year and we will use it for *in-situ* WF_6 calibrations of the UMD TMFCs.

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9. *Quantitative Optical Measurements of Gas Partial Pressures*

***J.P. Looney**, R.D. van Zee, and J.T. Hodges*

Objective: To develop measurement standards for partial-pressure measurements of low-level gaseous contaminants, with particular emphasis on H_2O, CO_2, CO, O_2, and CH_4.

Problem: Low-level gaseous contaminants cause deleterious effects in many chemical processing systems and drive the demand for improved measurement instrumentation and capabilities, as well as the primary standards that underpin measurement accuracy and reliability. As an example, the SIA NTRS identifies water vapor measurements as one of the key metrological parameters for contamination-free manufacturing in the next generation of devices, with a stated measurement capability of 100 ppt_v ng/g by the year 2001. Traditional techniques for generating low partial pressure standards for active gases, including water, are severely limited due to surface interactions and long time constants. Furthermore, the technical approaches used in the development of existing standards for vacuum and humidity are not capable of meeting many of the identified industrial measurement requirements. The development of a fundamentally new approach to this measurement problem is required.

Approach: The objective of this research is to develop quantitative high-sensitivity optical measurements and to establish a new primary standard for low-levels of gaseous contaminants. cavity ring-down Spectroscopy (CRDS) has been identified as the most suitable approach. The centerpiece of CRDS is a state-of-the-art, high-Q Fabry-Perot etalon. The Q of the cavity is determined by measuring the time constant for photon decay of an injected light pulse. The introduction of an absorbing species into the cavity degrades the cavity-Q and is a measure of the gas absorption and hence concentration. Recent advances in the high quality mirrors used to form the optical cavity have enabled realization of this measurement. Using these mirrors, cavities with Q's as high as 10^{10} have been constructed, for which ultimate water partial pressure sensitivities below 10^{-6} Pa (100 ppt_v) are projected.

Results and Future Plans: Building on our previous accomplishments, during this year we have implemented a unique variant of CRDS and developed a sound foundation for standards-grade pressure measurements. Combining our previously developed theoretical models, unique light source, and specially designed ring-down cavities, we have been the first group to demonstrate high sensitivity levels achievable using single-cavity mode ring-down spectroscopy with pulsed lasers. Optical ring-down signals can be measured with an standard deviation of 0.02 % to 0.05 %, about a factor of 4 to 10 larger than the ultimate levels achievable (the shot-noise limit). From these measurements, we have demonstrated an absorption sensitivity of $\approx 10^{-10}$ cm^{-1} in a 10 cm long cell, a 20-fold improvement in sensitivity of our unique approach compared to any other prior CRDS measurement.

A complete statistical analysis of the measurement imprecision was undertaken, and the noise sources that contribute to the overall pressure measurement uncertainty were delineated, quantified, and minimized. As a result of this effort, we succeeded in demonstrating a pressure measurement or integrated line-strength measurement imprecision of < 0.3 %.

Our detailed analysis of the noise sources in our measurements motivates some further refinements to our experimental approach and apparatus during the coming year. The primary refinement would be to develop a method for more precisely tuning the ring-down cavity. This refinement would potentially lead to lower imprecision in pressure and line-strength measurement. This, in turn, would provide a pathway to CRDS measurements with an imprecision competitive with prevailing primary pressure and vacuum standards in the vacuum and low-pressure range (10^{-5} Pa to 10 Pa).

Publications:

Looney, J.P., Hodges,J.T., and van Zee, R.D., "***Quantitative Absorption Measurements Using Cavity-Ringdown Spectroscopy with Pulsed Lasers,***" in Cavity Ringdown-Spectroscopy: A New Technique for Trace Absorption Measurements, K. A. Busch and M. A. Busch eds., American Chemical Society, 1998.

van Zee, R.D., Hodges, J.T., and Looney, J.P., ***"Measuring Pressure using Cavity Ring-Down Spectroscopy,"*** Proceedings of SPIE 3535 (1999).

Looney, J.P., van Zee, R.D., and Hodges, J.T., ***"Single-Mode Cavity Ring-Down Spectroscopy for Lineshape Measurements,"*** in Spectral Line Shapes 10, R.M. Herman, ed. AIP Press, 1999.

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10. Standards for Low Concentrations of Water Vapor in Gases

*J. T. **Hodges**, P. H. Huang, G. E. Scace, B. W. Mangum and D.C. Hovde (Southwest Sciences)*

Objective: To provide absolute standards for water vapor generation and measurement in the concentration range 1 nmol /mol to 1000 nmol/mol of gas.

Problem: Strict monitoring and control of trace levels of water vapor in carrier gases (1000 nmol/mol or lower) is required in numerous industrial processes related to the fabrication of microelectronics, photonics, and semiconductors. Regrettably, metrology-grade standards are not well established in this range, and existing hygrometers are inadequate as they often suffer from hysteresis, irreproducibility and relatively slow response. Further, measurements of low levels of water vapor are complicated by poorly understood interactions between the water vapor, carrier gases, and transfer lines, as well as uncertainty in thermodynamic properties of water vapor and carrier gas mixtures.

Approach: Two types of precision water vapor generators are being investigated: Type I, or thermodynamic-based systems, in which the delivered water vapor content depends on the mixture pressure and saturator temperature, and Type II, or permeation-dilution-based systems, based on empirically-determined water vapor permeation rates and measured gas dilution ratios. Prediction of the output of Type I generators requires knowledge of the vapor pressure of ice and other thermodynamic properties governing the non-ideal mixing of water vapor and carrier gas, two sets of properties having relatively small uncertainties. These uncertainties, however, become increasingly important as the water vapor content decreases. Type II generators are relatively simple to construct and easy to operate but suffer from the fact that their performance depends on gas flow rates and water permeation rates, two quantities that must be determined empirically and which are subject to long-term drift and potentially large uncertainty. A Type I generator is described below and constitutes the NIST working standard for the generation of low levels of water vapor. At present, generators of both types are being compared using various custom-made, as well as commercially-available and customer-supplied, hygrometers. International comparisons of NIST's Type I standard generator with those of other national standards laboratories also are underway. Sensors being investigated include chilled-mirror devices, optical absorption spectrometers, electrolytic and capacitive units, and vibrating crystal microbalance-type transducers, with the studies intended to quantify the stability and accuracy of precision generation systems and hygrometers.

Results and Future Plans: A new Type I generator was put into operation, and it is capable of delivering water-vapor concentrations down to approximately 3 nmol/mol, with long-term temperature stabilities of better than ±0.5 mK, and absolute accuracies of better than 10 mK in saturator temperature. Comparison of the new generator with another NIST Type I generator with a 25-year history indicates that in the region of overlap of the two systems, the two agree to within the stated uncertainty of the reference generator. The new Type I generator is now available to provide preliminary test services for clients desiring direct traceability to national standards of water vapor content. Although its precision is better than 0.2 %, the accuracy of the water vapor concentration in water/air mixtures generated by this standard is limited largely by uncertainties in the saturation vapor pressure of ice and the enhancement factor of the water vapor/gas mixture. These uncertainties are estimated to be on the order of 2 %. In an effort to experimentally determine the uncertainty, the generator output will be measured directly using gravimetric methods.

Recent measurements of the new generator output using a custom-designed hygrometer, based on laser absorption spectroscopy, demonstrated relatively fast time response, linearity over two decades of water-vapor concentration (in the range 3 nmol/mol to 3000 nmol/mol of water vapor), and high precision. Its calibration against the low frost point generator (LFPG) showed that background water vapor levels were less than 5 nmol/mol, and its response was within 5 % of that estimated from first-principles calculations. The laser-absorption hygrometer tracked the transient output of the LFPG during ramping of generator output, and statistically significant changes in the generated water vapor mole fraction as low as 0.25 nmol/mol were observable for averaging times less than 20 min. These experiments suggest that this highly sensitive hygrometer, known as the wavelength modulation spectroscopy (WMS) cell, will be ideal for measuring the difference between the output of an arbitrary test generator and that of NIST's Type I working standard generator.

As an independent check on the output of the Type I generators and to make measurements below the range of the gravimetric standard, we are developing absolute measurement techniques based on absorption of laser light by water vapor. These efforts involve the above-mentioned WMS cell and related systems that use the cavity ring-down spectroscopy (CRDS) technique. It is expected that such laser absorption methods will have sufficient sensitivity, dynamic range, and accuracy to provide a critical link between the primary gravimetric measurements of water vapor concentration made at relatively high concentrations and trace levels which cannot be determined gravimetrically. Preliminary experiments with WMS and CRDS indicate that accurate measurements of water-vapor concentration via laser absorption spectroscopy is a very promising method for measuring trace amounts, with sensitivities below the nmol/mol level. A long-term goal of this effort is to establish an absorption-based technique as a primary method of measurement, spanning several decades of water vapor concentration. In parallel with this effort, we are planning to extend the lower range of the Type I reference generator by at least an order of magnitude.

Publications:

Scace, G.E., Hovde, D.C., Hodges, J.T., Huang, P.H., Silver J.A., and J.R. Whetstone, ***"Performance of a Precision Low Frost-Point Humidity Generator,"*** in Papers and Abstracts from the Third International Symposium on Humidity & Moisture, National Physical Laboratory, UK, 1, 180-190, 1998.

Huang, P.H., ***"New Equations for Water Vapor Pressure in the Temperature Range 100 C to 100 C for Use with the 1997 NIST/ASME Steam Tables,"*** in Papers and Abstracts from the Third International Symposium on Humidity & Moisture, National Physical Laboratory, UK, 1, 68-76, 1998.

Scace, G.E., Hovde, D.C., Hodges, J.T., Huang, P.H., Silver, J.A., Whetstone, J.R., ***"The NIST Low Frost-Point Humidity Generator: A New Standard for Trace Humidity Measurement,"*** in Papers and Abstracts from the Workshop on Gas Distribution Systems, Semicon West 98, San Francisco, CA, J1-J9, 1998.

11. *Advancing NIST's Gas Flow Measurement Capabilities*

P. I. Espina, A. Johnson, G. M. Kline, P. I. Rothfleisch, D. B. Ward, J. D. Wright, and T. T. Yeh

Objective: 1) Demonstrate the feasibility of using information technology to expand NIST's calibration services via tele-presence in U.S. secondary calibration laboratories thus providing a framework for a new paradigm in calibration, traceability, and laboratory accreditation, and 2) reduce the uncertainty of NIST's gas flow standards by a factor of 4 over the range of 1 L/min to 100 L/min at standard conditions.

Problem: 1) Even though NIST provides calibration services over the better part of eight decades in flow, U.S. industry has critical needs for gas measurement traceability at much larger flow rates (ranging to approximately 10^8 L/min, three orders of magnitude larger than NIST's maximum flow rate), for high working pressures (up to 60 SI), and a gamut of gas species. A small number of secondary metrology laboratories in the U.S. are capable of calibrating gas flowmeters for these conditions, although with no direct flow-traceability to a national standard. However, the construction of national standards at NIST for these flow conditions would be prohibitively expensive and impractical.
2) In the 1 L/min to 1440 L/min range, CSTL presently provides gas flow calibrations using piston and bell provers (*i.e.*, volumetric devices) with expanded uncertainties of 0.20 % of reading. These standards were commissioned in the 1960s and, in spite of continuous upgrade efforts, their age and principle of operation hinder further improvements. Meanwhile, other U.S. secondary metrology laboratories, and several foreign national metrology laboratories, have developed gas flow standards with uncertainties in the 0.04 % to 0.08 % range. U.S. meter manufacturers are starting to produce flowmeters with uncertainties at or below the 0.2 % level. Without improvements in the NIST gas flow standards, the competitiveness of U.S. products in foreign markets is at risk.

Approach: 1) One way of expanding NIST's range of flow conditions is annexing existing secondary calibration facilities to NIST via tele-presence. Using this approach, NIST instrumentation would be installed in the remote calibration facility and, then we would assess the uncertainty of the upgraded facility. Following this, a communications and control structure would be added to enable remote operation and determination of *the complete metrological state* of the facility by NIST personnel. This determination, in the case of flow calibration facilities, requires consideration of both the flow source and the flow determination system. Primary flow determination systems typically are gravimetric or volumetric and present sensing technology readily lends itself to remote assessment. The same is not true of flow sources; however, we expect that non-contact flow measurement instrumentation can provide an *in-situ*, real-time monitor of the quality of the flow source and simultaneously serve as a check standard during calibrations.

2) We seek to develop an extremely novel, hybrid flow determination system, which will allow simultaneous gravimetric and volumetric determinations of the gas collected by the system. The resulting gravimetric-volumetric calibrator (GVC) will benefit from statistically independent measurements of the same quantity, thereby permitting greater confidence, and reduced uncertainty, in the final result. The design of the GVC emphasizes automation to enable unattended operation and to reduce operator bias.

Results and Future Plans: 1) As a first experiment and demonstration of this approach, we have selected a pressure-volume-temperature-time (PVTt) gas flow calibration system at the Colorado Engineering Experimental Station, Inc. (CEESI) in Nunn, CO. The plan calls for the technology to be developed and tested using the NIST PVTt system and then transferred to CEESI. To develop an *in-situ* monitor of the flow source and check standard for the meter under test, we are establishing a CRADA with Daniel Industries, Houston, TX, for the production of a NIST-designed, non-contact, multi-path ultrasonic flowmeter. We also are upgrading our PVTt facility – its automation-software, sensing systems, and strategies for remote operation – in order to demonstrate the tele-calibration concept before extension to CEESI. A workshop was held on November 19, 1998 in which we discussed our tele-calibration plans with other national and international flow metrologists.

2) Gravimetric and volumetric calibration methods were studied both by literature review and labora-

tory visits in the U.S. and abroad. National metrology laboratories in England, Germany, Japan, the Netherlands, and Spain were visited. Based on these reviews a detailed design for the volumetric elements of the GVC was made. Construction of the GVC began in the second quarter of FY98 with the purchase of the instrumentation and equipment needed for the implementation of the volumetric flow determination system. At present, the design calls for the volumetric elements of the GVC to simultaneously make use of PVTt and rate-of-rise (RoR) methods in the determination of the mass flow rate. Initial results indicate that the 0.05 % expanded uncertainty goal for the system is attainable. Future plans include the incorporation of gravimetric techniques and the expansion of similar technology to higher flow ranges.

Publications:

Wright, J. D. and Mattingly, G. E., "***NIST Calibration Services for Gas Flowmeters: Piston Prover and Bell Prover Gas Flow Facilities***," NIST SP 250-49, August 1998.

Wright, J. D., Mattingly, G. E., Nakao, S., Yokoi, Y., Takamoto, M., "***Intercomparison Tests of a NIST Primary Standard with a NRLM Transfer Standard for Small Mass Flow Rates of Nitrogen Gas***" Metrologia, in press.

Wright, J. D., "***The Long Term Calibration Stability of Critical Flow Nozzles and Laminar Flowmeters,***" NCSL Conference Proceedings, Albuquerque, NM, July 19-23, 1998.

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12. *Fluid Mechanics and Flow Metering Research*

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

Objective: To expand our capabilities for applying Computational Fluid Dynamics (CFD) to flow measurements, to improve the accuracy of existing flowmeter technology, and to develop new primary measurement methods.

Problems: Flowmeter accuracy can be highly dependent on installation conditions. Since very long straight lengths of constant diameter pipe are required to achieve "fully developed, ideal" pipe flow conditions, it is rare that these are achieved in metering practice. Therefore, unless meters are calibrated in their specific pipe work and under actual flow conditions, accuracies can deviate markedly from desired performance. This situation is prevalent in many industries but it can be very serious for large pipe sizes where it is not feasible either to calibrate specific pipe and meter arrangements in flow labs or to duplicate the typically high Reynolds numbers.

Approaches: Current advances in ultrasonic technology and in CFD provide potential solutions. Ultrasonic metering methods have the potential to serve as transfer standards which, for example, could be clamped on the outside of pipes to calibrate installed meters, and they can feasibly serve as primary standards to greatly improve our abilities to establish and to disseminate references for flow measurement. We have significantly improved our CFD capabilities by completing a program to apply compressible turbulence modeling to industrial flow problems and to modeling gas flows in important types of meters, such as critical nozzles, which are widely used as transfer standards. We can apply incompressible CFD capabilities to simulate the performance of a range of ultrasonic techniques that have potential to benefit wide ranges of flow measurements in U.S. industry. Additionally, we have initiated a collaborative program with industry to test commercially available travel-time, ultrasonic meters to assess performance potential in "ideal" and "non-ideal" installations and to complement our simulations.

Results and Future Plans: We have extended our CFD modeling capabilities to assess the effects of gas composition on the performance of critical nozzles. These widely used and highly regarded devices serve both as stable flowmeters as well as flow controllers. However, these devices are influenced by the boundary conditions (velocity and temperature) and the gas composition. Our study enhanced considerably the understanding of these flows and quantified these effects on discharge coefficients. The CFD results agreed well with experimental data except in the case of CO_2; vibrational-energy relaxation effects on gas density are thought to be the cause for the differences found in small nozzle geometries. Continued studies are planned to further advance our understanding of the salient factors that affect the performance of these devices, especially for small nozzles where subsonic throat boundary layers can constitute relatively large percentages of the cross-sectional area of the conduits, thereby producing "soft-criticality" characteristics that impair performance.

In FY98 we reported the results of our water flow-testing program to assess ultrasonic technology for its potential for improving flow measurement. This effort focused on clamp-on type, travel-time, ultrasonic techniques and quantified the performance of commercially available meters in ideal installation conditions: data analysis benefited from the computer simulations reported last year. The five participants calibrated their units, brought them to NIST, and installed them so that we could quantify each unit's optimal performance in the selected test conditions. Test results showed reproducibilities that ranged up to 3 %, with 3 units having 1 %, or less. Accuracies for most of the units ranged from –1 % to +3 % relative to NIST's flow standards. These offsets could be reduced through a NIST calibration so that performance could be specified in terms of the 1 % or better reproducibilities. These results showed that manufacturers have progressed well in solving previous difficulties involving "remove-replace" variations and the requirement of a "zero flow" condition to attain acceptable measurement performance. Further testing will quantify the performance of these units in non-ideal installation conditions downstream of an elbow.

We have continued computer simulations of travel-time ultrasonic techniques for measuring flow, especially in non-ideal installation conditions. We are examining "bounce" modes of operation. Our results for a range of reflected transmissions along angled diametral and chordal paths indicate that just downstream of an elbow, measurement errors can be reduced by 50 % or more using specific, angled diametral transmissions. Furthermore, multiple reflected chordal paths show promising results for detecting axial vorticity, or "swirl" in essentially real-time. We plan to continue these efforts to further advance our understanding of travel-time techniques for improving flowmetering, for designing effective flow transfer standards, and, possibly, for evolving these techniques into the status of primary flow standards based on length and time measurements. If this evolution occurs, it will enhance greatly our abilities to scale our flow standards to conditions far beyond the limited ones we can produce in our laboratory. Such a result could make flow measurement traceability to national or international standards a reality readily achieved.

Publications:

Yeh, T.T. and Mattingly, G.E., ***"Ultrasonic Flow Measurement Technology: Prospects for Transfer and Primary Standards,"*** in Proc. of the FLOMEKO '98 Confr. in Lund, Sweden, June 1998, 161-167.

Johnson, A.N., Espina, P.I., Mattingly, G.E., Wright, J.D., and Merkle, C.L., "***Numerical Characterization of the Discharge Coefficient in Critical Nozzles,"*** Procs. National Conference of Standards Laboratories Conference, Albuquerque, NM, July, 1998.

13. *Liquid Density Standards*

***V.E. Bean** and J.F. Houser*

Objective: Develop and dessiminate liquid density standards.

Problem: Commercially available liquid densimeters may have resolutions approaching a few parts per million, however, these instruments are not primary and require calibration.

Approach: Liquid density SRMs provide a means to calibrate densimeters and a NIST traceability linkage for industrial and other agency users. Toluene and isooctane samples are SRMs whose density values were perviously certified based on picnometry measurements. New batches of these hydrocarbons will be certified using hydrostatic weighing techniques that involve the NIST single crystal silicon density standards.

Results and Future Plans: As a proof test of our apparatus and methods, we measured the density of distilled water in tests comprised of six determinations per day on each of three days with a new water sample employed each day. The average of the 18 measurements is within 0.4 μg/g of the accepted valued for distilled water density. The expanded uncertainty of our approach is 4 parts per million.

The density measurements for toluene were finished during FY98. Two types of measurements are necessary:

a) the density of ≈1.5 L of toluene is measured hydrostatically, and,
b) the toluene from the 1.5 L ampoule is used to calibrate the comparator which is then used to measure the density of the toluene from a statistically significant number of 5 ml ampoules.

The 5 ml and 1.5 L samples are from the same batch of toluene and were ampouled at the same time. Statisticians in Division 898 for assessment of the final uncertainty are examining the data.

14. *Measurements and Models for Plasma Processing of Semiconductors*

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Objective: Develop advanced chemical and electrical measurement methods and models needed to characterize plasma etching and deposition processes important to the semiconductor industry, enabling continued progress in process optimization, process control, and model-based reactor design.

Problem: Plasma processing reactors have historically been designed and operated using empirical methods alone, but continued evolution of these tools requires a much greater reliance on process and reactor modeling. Indeed, model-based process design and control is a need identified in the *National Technology Roadmap for Semiconductors*. To obtain more reliable predictions of the spatial uniformity, chemistry, and electrical properties of processing plasmas, further progress in model development and validation is required. Also, to enable improvements in process control, a need exists to develop sensors that are compatible with the manufacturing environment.

Approach: Our experimental program has made use of reference reactors as testbeds for validating models and testing new measurement techniques. The reactors, known as Gaseous Electronics Conference Radio-Frequency Reference Cells (GEC Reference Cells), provide a well-defined basis for comparison of measurements between laboratories. The cells are equipped with a wide variety of plasma diagnostic tools that measure the chemical, physical, and electrical properties of the plasma. Information provided by the set of diagnostics allows testing of models. Also, sensors designed for manufacturing environments can be installed on the cells and compared with diagnostic results.

Results and Future Plans: Work continues on the development of sensors for real-time monitoring of ion current and ion energy in plasma reactors. At present, the development of rf-based ion current and ion energy sensors is limited by a lack of validated models for the electrical properties of plasma sheaths. This year, a new model of ion dynamics in the sheath region was developed and implemented in computer code. This model, which explicitly includes time varying ion currents, predicts the sheath electrical properties more accurately than existing (constant ion current) sheath models. Further tests of the model and use of the model in new, more accurate sensing techniques are planned for 1999.

We continue to investigate 2-D species densities in the GEC Reference Cell using 2-D planar laser-induced fluorescence (PLIF) imaging. In these studies, the concentration of CF_2 in fluorocarbon etching and chamber-cleaning plasmas is monitored as a marker of uniformity and chemistry for validation of 2-D plasma models. Results from previous years indicated that plasma spatial characteristics were correlated with the path taken by rf current flowing through the plasma. In studies performed this year, we were able to control the current flow and the plasma spatial uniformity using a variable impedance load attached to one electrode. The results suggest that this control method could aid in the optimization of chamber-cleaning plasmas. In 1999 we plan to extend our PLIF work to study etching plasmas in a high-density, inductively-coupled GEC cell. Experiments are also planned in a new research reactor, now under construction, which is designed to mimic state-of-the-art industrial reactors for 300 mm wafers.

Perfluorocompounds (PFCs) emitted by plasma reactors are global warming gases. In a continuing collaboration with Air Products and Chemicals, Inc., the destruction efficiencies of PFCs in chamber cleaning plasmas were measured, and the fundamental factors that limit destruction efficiencies were investigated. Also, we continue to support U.S. industry's drive to establish standards of practice for sampling and measurement of (PFC) emissions from plasma reactors and the metrics required to evaluate the reduction technologies. At the request of the Semiconductor Industry Association (SIA) draft reports were prepared and presented to the Environmental, Safety & Health Task Force of the World Semiconductor Council (WSC).

Publications:

Sobolewski, M.A., ***"Measuring the Ion Current in Electrical Discharges Using Radio-frequency Current and Voltage Measurements,"*** Appl. Phys. Lett. 72, 1146-1148 (1998).

Sobolewski, M.A., ***"Novel Ion Current Sensor for Real-time, In-situ Monitoring and Control of Plasma Processing,"*** Proceedings of the 1998 International Conference on Characterization and Metrology for ULSI. Gaithersburg, MD (1998).

Steffens, K.L., and Sobolewski, M.A., ***"Spatial Uniformity in Chamber-Cleaning Plasmas Measured Using Planar Laser-Induced Fluorescence,"*** Proceedings of the 1998 International Conference on Characterization and Metrology for ULSI. Gaithersburg, MD (1998).

Sobolewski, M.A., Langan, J.G., and Felker, B.S., ***"Electrical Optimization of Plasma-Enhanced Chemical Vapor Deposition Chamber-Cleaning Plasmas,"*** J. Vac. Sci. Technol. B 16, 173-182 (1998).

Green, D. S., ***"Dielectric Gases in the Semiconductor Industry: Applications and Databases,"*** Proceedings of the 8th International Symposium on Gaseous Dielectrics. Virginia Beach, VA (1998)

Green, D.S., and Meyers, J., ***"Characterization of PFC Emissions from Semiconductor Process Tools,"*** Proceedings of the U.S. EPA Global Semiconductor Industry Conference on PFC Emissions Control. Monterey, CA (1998).

Sobolewski, M.A., ***"Experimental Test of Models of High-Plasma-Density, Radio-Frequency Sheaths,"*** Phys. Rev. E, in press.

15. Models and Data for Semiconductor Processing

R. W. Davis, D. R. Burgess, Jr., M. J. Carrier, E. F. Moore, J. Maslar, M. R. Zachariah, W. Tsang (838), and R. Axelbaum (Washington Univ.)

Objective: To provide the necessary information and scientific infrastructure to enable the application of semiconductor process models and controllers that are well grounded in fundamental chemical and physical laws.

Problem: Reactor and process design are often limited to empirical trial and error approaches that tend to converge slowly, if at all, to semi-optimized states. This implies that, for an industry where rapid changes are the norm, important processes are not adequately investigated prior to final implementation. This situation manifests itself in more expensive, lower quality products produced by processes that may be less environmentally acceptable.

Approach: Process simulation has the potential to significantly enhance the design phase of process development so as to improve both efficiency and quality. This is because computational power has evolved to the point where highly sophisticated models can be constructed for a variety of complex semiconductor processes. However, the increasing complexity of these models implies a greater need for accurate fundamental thermochemical and kinetic data, which are not presently available. Our approach is both to develop and use methods for reliably generating (from first principles) the data necessary for process modeling. Techniques for handling, collating, and disseminating this information in an efficient and timely manner are an important component of this task. The reliability, quality, and utility of the generated data must also be demonstrated to the user community. Consequently, the development of process models of wide applicability is essential, as is model validation carried out in reference reactors prototypical of industrial processing equipment. This typically requires the development of reacting flow computer simulations that employ the aforementioned data for input.

Results and Future Plans: Our effort in the area of microcontamination in CVD reactors continued with the further development of the existing moment transport aerosol model for contaminant formation and transport in a rotating disk reactor. Various minor refinements were made to this model, and modifications were undertaken that allow particles entering at the reactor inlet to be tracked. This will provide crucial support to the initial phase of the complementary experimental effort in which the measurement system will be tested on injected particles with known characteristics. Additionally, the development of a second aerosol model for this reactor configuration was initiated. This effort is being undertaken by Dr. Richard Axelbaum of Washington University and will utilize a Monte Carlo or sectional approach in an attempt to construct a more fundamental model with fewer assumptions than the existing model. The use of two different types of models will provide enhanced synergy for the entire numerical/experimental effort.

An experimental rotating disk CVD reactor apparatus was assembled with equipment to measure both elastic and inelastic light scattering. *In-situ* nitrogen rotational Raman scattering spectra were measured in order to determine gas-phase temperatures in the reactor for various sets of operating conditions. Comparisons between experimental temperature profiles and those calculated from the one-dimensional model were good but highlighted the need for careful selection of operating parameters in order to obtain essentially one-dimensional experimental flows. Further temperature measurements and initial particle measurements on injected and, ultimately, gas-phase generated particles will be performed during FY99.

Our work in database compilation for chemical species of importance in semiconductor processing continued. The addition of thermochemical data for silicon oxyhydrides to our web site (http://www.nist.gov/cstl.div836/ckmech) was brought close to completion. During FY99, this work will be completed and chemical kinetic data (complementing the thermochemical data previously assembled) for silicon hydrides will be researched and made available.

Publications:

Davis, R. W., Moore, E. F., Burgess, D. R. and Zachariah, M. R., ***"A Microcontamination Model for Rotating Disk Chemical Vapor Deposition Reactors,"*** in Proceedings of the 1998 International Conference on Characterization and Metrology for

ULSI Technology, American Institute of Physics, (in press).

Babushok, V. I., Tsang, W., Burgess, D. R., and Zachariah, M. R., "***Numerical Study of Low and High Temperature Silane Combustion,***" in Proceedings of the 27th International Symposium on Combustion, The Combustion Institute (in press).

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16. Synthesis and Characterization of Nanostructured Materials

M. R. Zachariah, M. Aquino-Class, M. J. Carrier, N. Gorchkov (Guest Researcher), J. H. Hendricks, C. Scurlock (Washington Univ.), R. D. Shull (MSEL), and R. Axelbaum (Washington Univ.),

Objective: To develop a knowledge base for vapor-phase processing of nanostructured materials including both particulates and thin films.

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

Approach: Our approach has been to systematically study methods for the synthesis of nanostructured materials in both particulate and thin-film form, with an emphasis on methods that have the potential to be extended to the production of materials on a large scale. The vapor-phase route has been pursued as potentially the most robust generic method for producing quality materials in a cost-effective manner. There are two synergistic approaches being pursued: 1) development and investigation of new methods and chemistries for materials production; 2) application of advanced *in-situ* diagnostics for characterization of these processes in conjunction with the development and application of molecular-level models for predicting nucleation and growth of nanoscale materials.

Results and Future Plans: This year we continued our study of a new low-temperature (610 °C vs. 900 °C to 1200 °C for conventional CVD) environmentally-benign method for depositing Ti and TiN thin films utilizing sodium vapor reacting with a metal halide such as $TiCl_4$. The process parameters (pressure, reactant concentrations, substrate temperature, etc.) were varied in order to determine conditions for which essentially salt-free films could be produced at optimum growth rates. The thin films were analyzed by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), Raman spectroscopy, and wavelength dispersive spectroscopy (WDS). Process parameters were determined that resulted in growth rates of 0.15 μm/h with salt by-product concentrations of only 0.1 % by weight. These results were consistent with our thermodynamic calculations that predicted substrate temperatures below which salt deposition becomes problematic. We believe that this class of chemistry is generic, i.e., that a wide range of metal and ceramic thin film materials can be grown with this process by selecting from a variety of metal-halide precursors. Preliminary experiments have shown that this is the case for SiC and TiC films, and production of films from such superhard materials as CN and BN may also be possible via this process.

In our continuing computational investigations into the fundamental properties and kinetics of nanoparticles, we have concluded our studies into the growth kinetics of silicon nanoparticles using molecular dynamics (MD) simulation methods. The results have included the sensitivity of particle coalescence to both temperature and size, and for the first time, phenomenological models for such processes have been validated. In addition, we have been able to demonstrate the mechanisms of particle growth from an atomic level perspective. We believe that these results provide persuasive evidence of the power of the MD approach in not only defining and developing appropriate phenomenological models but also in elucidating the fundamental underlying physics of nanoparticle coalescence.

Publications:

Hendricks, J. H., Aquino, M. I., Maslar, J. E. and Zachariah, M. R., ***"Metal and Ceramic Thin Film Growth by Reaction of Alkali Metals with Metal Halides: A New Route for Low-Temperature Chemical Vapor Deposition,"*** Chem. Mater. , 10, 2221-2229 (1998).

Gorchkov, N., Aquino, M. I., Shull, R. D., Shapiro, A. and Zachariah, M. R., ***"Formation of an Iron/Salt Magnetic Nanocomposite by Vapor Phase Reaction of Sodium with Iron Chloride,"*** Nanostructured Materials (in press).

Zachariah, M. R. and Carrier, M. J., ***"Molecular Dynamics Simulation of Nanoparticle Coalescence: Comparison with Phenomenological Models,"*** Journal of Aerosol Science (in press).

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17. Self-Assembled Monolayers for Diagnostics and Sensing

M. Tarlov, T. Herne, G. Poirier, R. Levicky (NRC Postdoc. Assoc.), A. Steel (NRC Postdoc. Assoc.), C. O'Connell (831), G. Gillen (837)

Objective: Use self-assembled monolayers (SAMs) as model systems to develop fundamental, quantitative knowledge of generic molecular recognition and sensing reactions of ultrathin films. Develop and apply ultrathin film measurement methods to correlate molecular-scale structure of films with their diagnostic and sensing performance.

Problem: Biosensors and diagnostics are being developed to perform multi-analyte measurements rapidly, accurately, and at low cost. One promising approach is to use surface-confined arrays of highly selective sensing elements. For example, arrays of immobilized single-stranded DNA (ssDNA) probes, so-called DNA chips, may revolutionize genetic analysis for health care, toxicology, forensics, industrial processing, and environmental monitoring. While the feasibility of this technology has been demonstrated, there is still little known about factors such as molecular conformation and structure that influence hybridization of surface-bound probes. A fundamental knowledge base of surface hybridization reactions must be established for greater acceptance of DNA chip devices. It is also expected that new strategies for improving the sensitivity and selectivity of surface-bound probes in biochip applications will evolve from a greater fundamental understanding of these systems. To achieve this goal it will be necessary to develop *in-situ* measurement methods for correlating the structure of biomolecular layers with their molecular recognition properties.

Approach: Alkanethiol SAMs impart chemical sensitivity to Au surfaces by forming stable, ordered structures with highly tunable surface chemical and physical properties. The thiol headgroup bonds strongly to the Au surface, forming a densely packed monolayer where the functional group on the opposite end of the molecule forms the SAM surface. Biologically active films are prepared by derivatizing a biomolecule of interest with a thiol group, and then self-assembling the thiol-modified biomolecule on Au. Our studies are currently focused on establishing a detailed molecular-level picture of thiol-derivatized ssDNA monolayers. The surface density, hybridization activity, and molecular conformation of the surface-bound DNA probes are characterized with a variety of surface-sensitive methods, including electrochemical techniques, neutron reflectivity, grazing angle FT-IR, surface plasmon resonance, ^{32}P radiolabeling, X-Ray photoelectron spectroscopy, ellipsometry, surface-enhanced Raman spectroscopy, scanning tunneling microscopy (STM), and secondary ion mass spectrometry.

Results and Future Plans: Investigations in FY98 focused on establishing a detailed structural model of DNA probe monolayers and developing *in-situ* methods for quantifying the surface density of DNA. DNA conformational information was obtained from concentration profiles of DNA monolayer films determined *in-situ* with neutron reflectivity (NR). To our knowledge, these studies represent the most rigorous structural determination of DNA-functionalized surfaces to date. The NR results establish that the DNA conformation and activity are largely controlled by the self-assembly protocol that is used. By self-assembling a passivating monolayer of mercaptohexanol after adsorption of the thiol-derivatized ssDNA, a probe layer is formed where DNA molecules are exclusively end-tethered and hybridization efficiencies of nearly 100 % are observed. Following hybridization, the double-stranded DNA helices are observed to orient preferentially perpendicular to the plane of the substrate. We believe the perpendicular orientation results from geometric packing constraints of the DNA helices on the surface.

To quantify the surface density of DNA immobilized on Au, a sensitive electrochemical method, chronocoulometry, was applied. In this measurement process, a cationic redox molecule binds electrostatically and quantitatively to the anionic phosphate groups of the DNA backbone. The amount of the charge compensating redox molecule in the DNA monolayer, proportional to the number of phosphate residues and thereby the surface density of DNA, is measured using chronocoulometry. This method allows quantitative determination of both single- and double-stranded DNA at electrodes with a detection limit of 10^{11} DNA molecules/cm^2. The hybridization efficiency of immobilized DNA probes was measured as a function of surface probe density and found to exhibit a maximum with increasing surface density. These results define an optimal DNA probe coverage for maximizing assay sensitivity and minimizing DNA probe waste. Future studies will focus on *in-situ* surface plasmon resonance measurements of surface hybridization reactions with the aim of correlating kinetic behavior with surface molecular architecture. Factors to be examined include base pair mismatches and target sequence length.

STM was also used to elucidate the molecular packing of alkanethiol monolayers in an effort to correlate the nanometer-scale structure of SAMs with the macroscopic chemical and physical properties important in sensing and diagnostic applications. The mechanism by which thiols organize into monolayers was determined from molecular-resolution STM topographs obtained in real time during gas phase dosing experiments. The self-assembly of alkanethiols on Au was determined to be a complex process involving at least six discrete phases with associated phase transitions.

Publications:

Levicky, R., Herne, T. M., Tarlov, M.J., and Satija, S.K., ***"Using Self-Assembly To Control the Structure of DNA Monolayers on Au: A Neutron Reflectivity Study"*** J. Am. Chem. Soc. 120 (1998) 9787-9792.

Steel, A.B., Herne, T.M., and Tarlov, M.J., "***Electrochemical Quantitation of DNA Immobilized on Au***" Anal. Chem. 70 (1998).

Poirier, G.E., ***"Structural Phases and Phase Transitions of Alkanethiol Monolayers on Au(111)"*** J. Phys. Chem. submitted (1998).

18. Gas Sensing with Micro-hotplate Sensor Arrays

R. Cavicchi, S. Semancik, C. Kendrick, R. Walton, J. Allen, J. Suehle (EEEL), T. McAvoy (Univ. of Maryland),, J. Ding (Univ. of Maryland), D. DeVoe, (Univ. of Maryland), B. Panchapakesan, (Univ. of Maryland),, J. Kelliher, (Microelectronics Research Lab of the Department of Defense.)

Objective: Demonstrate feasibility of silicon micromachined, thin-film sensor array technology for multi-analyte, real-time detection and concentration measurement of gases.

Problem: Increasing global competition has placed new demands on the chemical process industry for more efficient use of materials, better process reproducibility, and environmental safety. Similar measurement concerns are encountered in the automotive field where engine performance and reduced emissions are issues. Meeting these demands requires a low-cost technology for the measurement of gas species, which can provide immediate, on-site analysis for the detection of reaction products, exhaust gases, leaks, etc.

Approach: Advances in microfabrication technology now make possible miniaturization of conventional conductometric low-cost metal oxide sensors into a planar array form. At NIST, a sensor array platform has been developed that uses a "microhotplate" as the generic device structure. The microhotplate has three functional layers: a heater, a thermometer/heat distribution plate, and electrical contacts for monitoring the conductivity of sensing films. Devices are fabricated using CMOS processing combined with post-CMOS process silicon micromachining, and sensor film deposition. NIST holds three patents on this technology.

The most important challenge is to develop methods for fabricating and lithographically defining sensing films with the desired characteristics of sensitivity, selectivity, and stability. Catalyst-doped metal oxide materials, which have shown good sensing characteristics on the conventional sensors, must now be produced in a thin film form. Reactive sputter deposition and chemical vapor deposition (CVD) methods are adapted to take advantage of the self-heating of the micro-hotplates for thermally processing the sensing film. With CVD, varying the precursor composition and selecting which micro-hotplates in an array are activated, array elements with different materials can be produced.

Because of their 50 μm to 250 μm size the elements can be heated and cooled rapidly with time constants of one to two milliseconds over a large operating temperature range (>800 °C). This capability supports a novel sensing approach, temperature programmed sensing, (TPS). The effects that produce a response signal are based on thermally-activated processes such as adsorption, reaction, and desorption. By varying the temperature in a defined, repeated pattern using millisecond-scale temperature changes, the sensor generates response signatures that are characteristic of adsorbed species/sensing material combinations. Neural network and chemometric-based approaches are being used to optimize the generation of signatures and to analyze signals during sensing.

To advance sensing materials and methods, mechanisms behind the signal transduction process must be better understood. Depending on whether the thin film structure is polycrystalline or epitaxial, the dominant mechanisms may be related to grain-boundaries or the properties of the oriented-surface. The rapid temperature variations used to generate signals require a better understanding of the reaction kinetics. Surface analytical techniques combined with electrical measurements are used to address these issues.

Results and Future Plans: Improvements in the device platforms and fabrication methods continue to enhance the reproducibility and stability of micro-hotplate sensors. While designs for a new set of planar micro-hotplates were completed and sent to Lincoln Laboratories (MIT) for fabrication, development of better methods of sensor film processing using the tungsten-based devices fabricated at the Microelectronics Research Laboratories of the Department of Defense (MRL) continued. Sensing films are evaluated for gas sensitivity, stability, and selectivity in correlation with materials properties such as microstructure and composition. A set of three studies is underway: 1) a comparison of sputtered vs. CVD SnO_2 for sensing, 2) a comparison of the effects of a metal seed layer (Sn, Pt, Fe, Pd, etc.) on the CVD growth of tin oxide, and 3) a comparison of the use of different catalytic metals in combination with SnO_2. A process for patterning the various metal films was developed that circumvents difficulties related to performing photolithography on micromachined structures. This process uses a nitrocellulose coating that can be flashed off using a thermal pulse to the micro-hotplate heater. After deposition of the metal layer, liftoff removes the nitrocellulose and metal from all areas except the pulsed micro-hotplate. In related experiments, an electrochemical method was developed for depositing polymer sensing films.

Initial studies to assess the capabilities of the conductometric microsensors for identifying specific chemical products occurred during the last year. These experiments were done as part of a cooperative research and development agreement (CRADA) with the Dow Chemical Company. Under a new interaction with the Center for Process Analytical Chemistry (CPAC), University of Washington, principal component analysis was used to analyze SnO_2 sensor data. In this work, the sensor was successfully used as a detector in a gas chromatograph with test samples consisting of two-component mixtures. A collaboration with the University of Maryland continued to investigate the use of neural-net optimization methods with temperature programmed sensing to determine concentrations and to distinguish mixtures of two gases. The long tests required for modeling the sensor over a wide range of mixtures uncovered drift phenomena in the sensors which are now being investigated. Under a contract with the Defense Threat Reduction Agency, the suitability of microhotplate sensors for detecting chemical agents is being evaluated. A system for testing simulants of these agents is under construction, and tests will begin next year. A study of sensor materials for chemical sensors will commence next year under sponsorship of the Department of Energy Environmental Science Management Program.

Publications:

S. Semancik and R. E. Cavicchi, ***"Kinetically Controlled Chemical Sensing Using Micromachined Structures"*** Accounts of Chemical Research 31, (1998) 279-287.

C. E. Kendrick and S. Semancik, ***"Doping Effects and Reversibility Studies on Gas Exposed Alpha-Sexithiophene,"*** J. Vac. Sci. Technol. A16 (1998) 3068-3075.

T. Kunt, L. Ratton, T. McAvoy, S. Semancik and R. E. Cavicchi, ***"A Systematic Approach for Tuning Microhotplate Chemical Sensors,"*** Proc. of the 5th International Symposium on Identification and Quantification of Odors, in press.

19. Measurement Technology for Benchmark Spray Combustion Data

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Objective: Develop measurement technology to provide benchmark experimental data for input/validation of multiphase combustion models, optimization of process control architecture, calibration of instruments/sensors, and development of advanced diagnostics. Establish correlations between operating conditions and the resultant spray flame characteristics, thermal gradients, and level of chemical byproducts in combustion systems.

Problem: Control of process efficiency and the formation of species byproducts from industrial combustion systems (e.g., power generation and treatment of liquid chemical wastes), is relying increasingly on computational fluid dynamics (CFD) simulations to provide relevant process information in a cost-effective manner. However, there is a dearth of reliable data for specifying model initial/boundary conditions, and a need for experimental/numerical comparative analysis of conditions within the reactor. The need to provide benchmark data on the characteristics of the droplet field, flame structure, heat transfer, and particulate/gaseous byproducts, and its interrelationship with the system operating conditions (e.g., desired stoichiometry) is crucial for the development and calibration of advanced computational models, diagnostics, and instrumentation.

Approach: The NIST spray combustion test bed has evolved into a well-characterized and controlled system that can handle different 1) process liquid fuels and wastes, 2) atomizer designs, and 3) combustor configurations. A variety of diagnostics are employed or being developed to characterize the input fuel stream (fuel composition), spray flame (droplet size, velocity, and temperature), and flame emissions (particulates and chemical species). A coupled experimental/computational approach is used to involve modelers from our industrial partners directly in the program.

Results and Future Plans: Our efforts in FY98 focused on development of the benchmark experimental database for input and validation of multiphase combustion models that are used by our partners in industry (i.e., Dow Chemical, McDermott, StreamWise, Cabot, John Zink, CFD Research, and others), and academia. The experimental apparatus consists of a swirl burner enclosed within a stainless steel chamber to allow for better controlled operation of the system and reproducibility of the spray flame characteristics. In collaboration with our industrial partners, a baseline case was defined with well-defined initial and boundary conditions. A variety of diagnostic techniques were employed to characterize the boundary conditions and multiphase combustion processes within the flow field. Of particular interest are measurements of the spray characteristics, gas phase velocities, and chemical reaction byproducts. A two-component phase Doppler interferometer (PDI) was used to determine the concentration, size, and velocity of the fuel droplets within the methanol flame. Quantitative gas-phase concentrations (including condensable species) were determined using Fourier transform infrared spectroscopy. Thermocouples have provided gas temperatures along the chamber walls and across chamber exit.

Statistical uncertainties are provided with the experimental results so that the database provides the confidence levels needed, and to date lacking in the literature, for validation of developing and commercially available models. To this end, a collaboration were formed with the NIST Statistical Engineering Division to 1) determine the confidence levels in the size and velocity data, 2) develop fitting distributions functions for measured size/velocity distributions of both monomodal and bimodal forms, and 3) analyze detected structure in the droplet interarrival-time statistics.

Different fuel injector concepts are under investigation in an effort to develop a reference atomizer that will produce well-controlled size and velocity distributions, and provide known initial conditions at the injector inlet. One concept under development, in collaboration with Fluid Jet Associates, is an acoustically driven multi-orifice injector. Experimental results have shown that acoustic modulation generated uniformly-sized, and uniformly-spaced droplets. We also studied the effect of fluid properties (i.e., viscosity, density, and surface tension) on droplet formation processes (see reference). Ultimately, we plan to design plates with hole patterns that will form well-controlled sprays, representative of actual spray patterns, and serve as inlet boundary conditions for our benchmark spray combustion database.

In FY99, we plan to conduct a workshop to uncover additional measurement needs for development of spray combustion models, and define the next phase of this program.

Publications:

Chung, I.-P., Presser, C., and Dressler, J.L., ***"The Effect of Piezoelectric Transducer Modulation on Liquid Sheet Disintegration,"*** Atomization and Sprays, 8, No. 5,. 479-502 (1998).

20. Heat and Mass Transfer in Supercritical Processes

D.A. Olson, D. Allen (Geocenters), L. Ong, P. Domanski (BFRL), and J. Manzione (U.S. Army)

Objective: Develop measurement technology and acquire high-quality experimental data on the thermal and fluid mechanical performance of flowing supercritical fluids, which can be used to develop engineering design models.

Problem: Supercritical fluids have become increasingly important as alternative fluids in modern technologies such as precision cleaning, chemical synthesis and extraction, and as working fluids in refrigeration and heat pumps. Flow and thermal fields must be understood and predicted before chemical processes in these fluids can be modeled. Due to fluid properties that are very sensitive to temperature and density, these flow fields can be fundamentally different than those of liquids or low-density gases. Basic understanding of these processes is poor, resulting in a lack of predictive methods for the supercritical fluid processes.

Approach: Our approach is to carry out measurements on flowing supercritical fluids, and utilize the data to develop and validate computational fluid dynamics (CFD) models that incorporate the most accurate equations of state and transport properties for the fluid. By studying a variety of industrially relevant geometries over ranges of flow, thermal, and pressure conditions, we can explore the strong coupling between the non-linear fluid property variations and the large buoyancy forces that characterize supercritical fluid flows.

Results and Future Plans: We have first concentrated on flow through horizontal tubes, in which supercritical carbon dioxide is heated by the counterflow of hot water. This configuration is of great interest to the emerging carbon dioxide-based refrigeration community, which requires supercritical heat exchangers for their process. Waste destruction by supercritical water oxidation also requires this class of heat exchangers. This year we acquired an extensive set of experimental data on the flow of supercritical carbon dioxide in a heated horizontal tube. This was the first controlled experiment of its kind, in which the supercritical fluid was heated by exchange with another fluid, rather than by a constant heat flux heater. The results showed that for the supercritical fluid, the heat transfer effectiveness was enhanced (when compared to a pure liquid or low-density gas) for high Reynolds numbers and low amounts of heating. When the heating rate was high or the Reynolds numbers were low, the heat transfer effectiveness with the supercritical fluid was degraded. These effects were compounded when the operating pressure was closer to the thermodynamic critical point. An existing correlation, developed for constant heating of a supercritical fluid, was found to predict the measured data to within the experimental uncertainty.

We are currently calculating flow patterns for the horizontal tube using commercial CFD software and accurate fluid equations of state at the operating conditions of the experiment. These results will help us understand why the supercritical fluid has enhanced heat transfer performance for certain conditions and degraded performance for others. In FY99, we will acquire additional experimental data over a wider range of operating conditions and continue the development of CFD models. We will also continue fostering ties with industries using supercritical fluids, such as semiconductor cleaning and refrigeration.

Publications:

Olson, D.A., and Allen, D., ***"Heat Transfer in Turbulent Supercritical Carbon Dioxide Flowing in a Heated Horizontal Tube,"*** NISTIR 6234 (1998).

21. Standards for Raman Spectroscopy

W.S. Hurst, S.J. Choquette (Div. 839), and E.S. Etz (Div. 837)

Objective: Critically evaluate presently existing approaches and develop new methods and associated standards that will provide for calibration of the frequency and intensity axes of Raman spectral data.

Problem: It is widely acknowledged that major advances in analytical Raman instrumentation have virtually revolutionized Raman spectroscopic measurements. Raman spectroscopy is now finding its place in the industrial environment for process measurements and quality control. Calibration of both the signal intensity and wavelength axis are important. In Raman spectroscopy the intensity of the analytical signal is not calibrated as part of the measurement, unlike infrared (IR) spectroscopy. Consequently, relatively few published spectra have been corrected for the typical variations in the instrument response function, and there are no widely available standardized Raman spectral libraries. Intensity calibration is needed to make process-control Raman measurements instrument-independent, for component analysis of unknown mixtures, and for reliable and robust quantitation. Maintaining a highly-accurate wavelength calibration on all acquired spectra is needed if the training sets of multivariate analyses used in process control algorithms are to maintain their validity. With increasing use of diode lasers, it is also needed for determination of excitation frequency. The lack of accepted practices, standards, and spectral libraries is the main obstacle to acceptance of Raman in industrial settings and a barrier to its use in regulated industries.

Approach: In response to the Raman community's need for practical standards for analytical Raman spectroscopy, two approaches for the calibration of the intensity are under consideration. The first will employ a method for intensity calibration using fluorescent materials. NIST will evaluate this method and will collaborate with Richard McCreery of Ohio State University who was the first to have proposed this approach. NIST will research the choice of fluorescent materials by evaluating the fluorescence spectra of rare-earth doped glasses to provide both broad-band and narrow-band emissions over the common Raman spectral domains. These glasses will lead to the certification of a set of SRMs traceable to NIST primary radiometric standards. While fluorescence can be exploited for intensity calibration, a more fundamental approach rests upon the determination of absolute Raman cross sections to provide an absolute intensity calibration that is verifiably instrument-independent. A Raman gain spectrometer will be developed for the measurement of the Raman cross sections of judiciously chosen liquids and solids that may serve as absolute Raman intensity standards. Frequency calibration issues will be studied, with cooperation as needed with the ASTM effort to establish Raman peak positions of selected compounds. Contact with the Raman community, major chemical industries, instrument manufacturers, regulatory agencies, and initiatives adopted by the ASTM E13.08 Subcommittee on Raman Standards, will be maintained so that methods, standards and techniques developed by NIST are widely accepted by the industry.

Results and Future Plans: In FY98, the first year of this program, a suite of glasses bearing one or more rare-earth and transition metal elements were investigated for their Raman and fluorescence emissions. The glass matrices were borosilicate, phosphate and germanate glasses. They were investigated on three Raman systems, focusing on the Raman ranges defined by three excitation wavelengths (514.5 nm, 785 nm, and 1064 nm - the latter by FT-Raman). Three glass compositions have been identified as potential candidates for secondary Raman intensity calibration standards, having suitable broad-band emission over the desired Raman shift ranges. Evaluation of an intensity calibration method has been initiated at 514.5 nm, differing from the plan above by the use of a fluorescent dye rather than a fluorescent glass, with comparisons made with recent results obtained at Ohio State University. FY99 plans include further investigation of the glasses that have been identified as candidates in order to optimize the glass compositions for fluorescence and to test their usefulness as calibration standards. Several of the laboratories (industrial and university) represented on ASTM E13.08 will also do some initial evaluations on these materials. Evaluation of the use of fluorescence as a calibration technique will be extended to include several spectrometers at NIST, using several excitation wavelengths.

IV. Surface and Microanalysis Science Division (837)

Rance A. Velapoldi, Chief

A. Division Overview

***Mission*:**
The Surface and Microanalysis Science Division serves as the Nation's Reference Laboratory for chemical metrology research, standards, and data to:

- Characterize the spatial and temporal distribution of chemical species; and
- Improve the accuracy, precision, sensitivity, and applicability of surface, microanalysis, and advanced isotope measurement techniques.

The Division provides the tools for the Nation's measurement communities to enhance U.S. industry's productivity and competitiveness, assure equity in trade, and improve public health, safety, environmental quality, and national security. We perform research to:

a) determine the chemistry and physics of surfaces, interfaces, particles, and bulk materials, and their interactions with a broad spectrum of species including electrons, photons, ions, atoms, and molecules;
b) determine the chemical and isotopic composition, morphology, crystallography, and electronic structure at scales ranging from millimeters to nanometers;
c) determine the energetics, kinetics, mechanisms, and effects of processes occurring on solid surfaces as well as within materials and devices;
d) study the total chemical measurement process as well as source apportionment in atmospheric chemistry using advanced isotope metrology and chemometrics; and
e) develop and certify key Standard Reference Materials and Standard Reference Data.

Emphasis is placed on performing fundamental and applied measurement research to push the measurement envelope by anticipating measurement, standard, and data needs through interactions with a broad base of customers. This infrastructural information can provide the basis for advances in various technologies, such as chemical catalysis, advanced electronics and materials science and provides the tools that industry can use to solve their measurement problems.

This year, Division staff members focused on industrial interactions to better assess measurement, standards, and data needs, to fold those needs into current programs, and to assess impact of our research on their programs. In the past several years, our interactions with industry can be placed in two main categories. First, as scientists who push the state-of–the-art in measurements, we interact extensively with the companies that affect the state-of-the-practice, i.e., the instrument manufacturing and analytical consulting and service industries. Second, we apply the developed techniques to measurement problems of a broad range of companies that include the electronics, materials, and chemical industries. In the first case, we have had more than 15 interactions with industry to develop new sources, detectors, or software for microprobe analysis. For example, we are collaborating with Peabody Scientific to develop **a novel SF_5^+ ion source** that will provide increased sensitivity and resolution in molecular SIMS analysis.

In the second case, we provide a broad range of outputs and efforts including issuing SRMs and SRD; applying measurement capabilities to industrial problems; holding workshops or targeted sessions at conferences; and working with national and international organizations such as ASTM, ISO, IUPAC, and IAEA to develop widely promulgated standards. One example is the issuance of **SRM 2806 Medium Test Dust (MTD) in Hydraulic Fluid** and RMs 8631 Medium Test Dust (MTD) and 8632 Ultra Fine Test Dust (UFTD). These materials were developed in collaboration with the fluid power industry through **the National Fluid Power Association** (NFPA). These new measurement standards establish a previously unavailable accuracy base for determining contaminants in hydraulic fluid, a critical need. According to the NFPA, the "New NIST calibration material modernizes automatic particle counting." and companies will "…benefit from improved accuracy and reproducibility ... Standard will lead to more effective contamination control programs, lower operating costs, less downtime, and increased reliability." In a second example, we were able to apply our advanced instrumentation to solve measurement problems in several industries, other government agencies, and academia through telepresence microscopy and microanalysis over the World Wide Web. An objective for this year, is to identify a topic suitable for an economic impact study to expand the formal evaluation of our impact.

Division scientific staff pursued vigorous program planning activities in a number of new areas. These efforts covered a broad range of topics, from Fundamental Radical/Surface Reaction Kinetics, to Telepresence Microscopy and Microanalysis, to determining volatile organic compounds that are precursors to ozone formation. As a result the Division received new funding in several of these areas and is expanding its program in Nanoscale Chemical Characterization. This effort, *Characterization of Ultra Thin Films*, strengthens the Division's activities supporting the SIA National Technology Roadmap for Semiconductors. Objectives of the Division's programs and selected accomplishments are given below to provide a flavor of the research performed and of program directions.

Programs:

Nanoscale Chemical Characterization: Our objectives are to push the measurement envelope and provide infrastructural tools for the measurement communities to determine the chemical composition of various samples, at increasing spatial resolutions and decreasing concentrations. In a broader context, the measurements include the chemical characterization (elements, isotopes, and molecules) of materials at millimeter to nanometer and smaller spatial scales with major, minor, and trace chemical concentrations. In addition to determining qualitative and quantitative chemical composition, the measurements also include determining crystallography (species and molecules) and morphology (structure). Instrumental methods include electron, ion, photon, and X-Ray probes. These measurement tools can then be applied across a broad range of problems in the private and public sectors such that the '**micro-spatial' relationships of chemical species** can be correlated with **specific macroscopic properties** of high technology materials or electronic devices as well as to determine the effects of individual manufacturing steps on a system or product.

Selected Accomplishments:

- Developed a method using grazing incidence X-Ray photoemission spectroscopy to measure oxide layers with thicknesses less than 10 nm on semiconductor substrates and showed that the photemission behavior is in good agreement with theoretical predictions.
- Used Telepresence Microscopy and Microanalysis to solve measurement problems in industry, academia, and other government agencies.
- Proposed and obtained funding for a new program titled "Characterization of Ultra-Thin Films".
- Demonstrated, for the first time, the potential to identify chemical species based on spectral shifts using low energy electron probe microscopy and the new NIST Microcalorimeter detector.

Particle Characterization and Standards: Our objectives are to focus on the special case of individual particles or samples and provide measurement capabilities to 1) **characterize individual particles**, and 2) characterize a sample by the chemical composition of each particle summed into "**particle populations**," a micro to macro concept. In this concept, automated measurement methods are developed by optimizing sample and instrument measurement parameters, and developing or extending software for data collection, visualization, and interpretation. These methods are then used for the identification of samples, contaminants, or to analyze particle starting materials or products in advanced materials production as well as in the development of particle SRMs. We also apply these infrastructure measurement capabilities to characterize actinide and other materials of interest; develop standards, data, and measurement protocols appropriate for use in quality assurance by various laboratories; and transfer these measurement capabilities to the appropriate measurement communities, e.g., DoD, DoE, and IAEA. These latter efforts aid the Nation in monitoring the Comprehensive Test Ban Treaty and determining the spread of nuclear weapons, aid in deterring terrorism, and help the IAEA carry out their mission of worldwide nuclear monitoring.

Selected Accomplishments:

- Completed SRM 2806 Medium Fine Test Dust in Hydraulic Fluid and two Reference Materials, which were incorporated in ISO standards that are central to contamination control in the Fluid Power Industry.
- Developed and characterized a method for measuring the fractal dimensions of particles.
- Determined the heterogeneity and chemical microstructure of tungsten carbide-cobalt powders to assess their potential utility as SRMs.
- Developed a novel approach using low-voltage, electron beam microanalysis to improve the accuracy of quantitative analysis by a factor of five for micrometer-sized particles.

Electronic and Advanced Materials Characterization: Objectives are to apply measurement techniques for the **chemical and morphological characterization** of electronic devices and components (e.g., semiconductors, superconductors, optoelectronics) and advanced materials (e.g., coatings, ceramics); and to develop needed standards and data. The projects chosen to demonstrate the application of our developed measurement techniques range from needs defined by the Semiconductor Industry Association (SIA) roadmap to determining contaminants in starting materials and finished products from various industries.

Selected Accomplishments:

- Used advanced electron microscopy techniques to determine the role of TiN-capping layers in improving the quality of silicide films in semiconductor production (with MIT/Lincoln Labs).
- Used Web-based Telepresence Microscopy and Microanalysis to speed identification and resolution of 100 nm contaminants in metal-silicon oxide interfaces.
- Collaborated with Lucent Technologies to increase the repeatability (from ≈10 %-15 % to 1.3 %) and accuracy (measured doses were 15 % lower than targeted doses) of ion implantation dose measurements using SIMS.
- Characterized diamond-like amorphous carbon films on Si and Mo substrates at ≈1 nm resolutions for use in flat panel (field emission) displays by EELS.

Chemical Measurement Process: Objectives are to investigate the Chemical Measurement Process and establish generic methods, standards, data, and definitions, as bases for overall quality assurance. Several aspects of these objectives are important aids to industry in **achieving ISO 9000 certification requirements** as well as providing the basis for traceability among national and international standards bodies, industries, and governments. Examples include: calibrations, data analysis/interpretation, process design, model validation, estimates of uncertainties and bias, Standard Reference Data (SRD, Standard Test Data (STD), Standard Reference Materials, and Documentary Standards (e.g., terminology and reference procedures).

Selected Accomplishments:

- Established a web-based service to provide interactive Standard Test Data for the XPS user community.
- Determined the nature and distribution of the chemical blank and its impact on low level and high-accuracy isotopic-chemical metrology
- Organized the 11th International Conference on Secondary Ion Mass Spectrometry
- Provided major contributions to IUPAC *Compendium of Analytical Nomenclature* as chapters labeled "Presentation of the Results of Chemical Analysis" and "Quality Assurance of Analytical Processes".
- Developed and issued SRM 1922: A Mineral Oil Refractive Index Standard for the calibration of refractometers, critical to the sugar industry

Surface and Interface Chemistry: The program develops measurement tools for the characterization of, provides fundamental data on, and produces models for, the basic chemical events that occur in surface and interface reactions. Laser and electron spectroscopies and mass spectrometry are applied to the study of **advanced surface processes** including photoreactions at surfaces, **energetic radical reactions with surfaces**, and the details of thin-film growth and surface structure formation. Optical probes are also used to study both **solid/solid** and **liquid/solid interfaces**.

Selected Accomplishments :

- Quantified anisotropic microstructure development during the reaction of Mg with GaAs using novel height-height correlation analysis.
- Implemented experimental facilities to study O-atom surface reactions in semiconductor processing.
- Characterized the reactions of H-atom with H_2O on Si with FTIR.
- Demonstrated for the first time the applicability of Broad Band Sum Frequency measurements for studying buried interfaces of SAMs on gold

Advanced Isotope Metrology: Objectives are to develop basic procedures and provide tools to measure isotope ratios **of chemical species in processes** such as combustion, atmospheric gas-particle interactions and transformations, and contaminant transport, all critical for atmospheric source apportionment. Included here are the general objectives for chemical species source apportionment:

1) apply isotopic and molecular chemical characterization techniques to measure atmospheric contaminants on local, regional, and global bases;
2) determine sources of the contaminants;
3) model results considering meteorology to develop optimum sampling locations and strategies; and
4) provide results to interested sectors so they can devise control strategies for pollutant or contaminant reduction.

Various emissions can be differentiated including woodburning, gas and diesel vehicles, power production, fast food frying, biomass burning, biogenic sources as well as chemical species used in or contaminants produced by manufacturing processes. Other isotope measurement capabilities include dual isotope dating, authentication, actinide analyses, and individual pulse characterization in low-level counting.

Selected Accomplishments:

- Developed and tested measurement procedures to determine the non-fossil fraction of VOCs and thus provided another tool to differentiate fossil from biomass sources as ozone precursors.
- Established protocols to enable accurate isotopic ratio mass spectrometry for Reference Materials.
- Applied multivariate isotopic fingerprinting to identify multiple feedstock sources and finished industrial materials to apportion sources among products with identical chemical compositions.
- Planned and collected combustion aerosols during the International Crown Fire Modeling Experiment in Canada's Northwest Territories to participate in developing advanced models of global climate change.
- Used advanced isotopic and chemical metrology to identify isotopic and molecular fractionation in combustion processes

Molecular Scale Chemical Characterization of Organic and Biomolecules: The critical dimensions of emerging technologies have shrunk to the point that current, infrastructural, **spatially-resolved surface-microprobes of molecules** and species cannot meet the projected chemical measurement needs of industry. The Division has addressed this challenge *via* the development of two categories of advanced, non-destructive surface probes. The first is to leverage the NSOM competence project into this robust program by developing **chemically resolved scanned probe microscopies** (e.g., chemical force AFM, heterodyne scanning tunneling microscopy (STM), and the SIMS/TOF-SIMS measurement methods. The second is to focus on the development of a project under the **Nanoscale Chemical Characterization** program to develop capabilities in spatially resolved AES and XPS. The molecular information from the scanned probes and SIMS techniques, and elemental and oxidation state information from the probes of electronic states, will provide complementary, information on surfaces of technological interest.

Selected Accomplishments:

- Demonstrated a near-field enhancement for Raman NSOM data which led to an *in-situ* method for tip characterization.
- Characterized and quantified the optical basis of NSOM tip-sample interactions through a combination of detailed measurements and advanced theoretical modeling.
- Demonstrated that non-contact AFM measurements of SAMs minimized tip induced damage to soft surfaces.
- Developed, in collaboration with Peabody Scientific, a new SF_5^+ source that provides increased sensitivity and spatial resolution in molecular SIMS

Other areas for future consideration as either new programs or emphasized major projects include **Chemical and Process Information for Surface Engineering** and **Source Apportionment of Important Chemical Species**.

Staff Recognition: Honors our staff received this year include: **Lee J. Richter** – Maryland Distinguished Young Scientist Award - in recognition of his detailed studies of photo-induced surface chemistry; **Robert A. Fletcher** – Department of Commerce Bronze Medal for "…leadership in all aspects of the development and issuance of reference materials for calibrating particle contamination monitoring devices"; **Group Award for Division 837 and 839** – Certificate of Excellence from the Department of Defense for the five year period 1992-1997 "In recognition of your exemplary contributions as a member of the Air Force Technical Applications Center Materials Product Team … leading to award of the National Defense Meritorious Unit Citation…..team distinguished themselves by providing exceptional support to …..the United States Air Force and Policy makers up to and including the President of the United States.", **Robert A. Fletcher, Jennifer R. Verkouteren, Eric S. Windsor, John A. Small, Eric. B. Steel, David S. Bright, Walter S. Liggett (ITL) and Robert J. Gettings (TA)** – CSTL Technical Achievement for "development and issuance of SRM 2806 - Medium Test Dust in Hydraulic Fluid and two associated Reference Materials RM 8631 and RM 8632".

Interactions: Strong interactions by the staff with our constituents and effective technology transfer are shown by substantial technical outputs, participation on 10 editorial review boards, close interactions with national (e.g., ASTM, ANSI, MAS, EMSA, NFPA) and international (e.g., ISO, IUPAC, IAEA, VAMAS) organizations, and participation on established committees. In addition, staff participated on evaluation and consulting panels for DoE, DoD, NSF, EPA, NRC, U.S.GS, WHOI, and industrial groups. Finally, we have organized, co-organized, or participated in several international and national conferences.

B. Selected Technical Reports

1. *Measuring Chemical Shifts in Electron-Excited X-Ray Spectra with the NIST Macrocalorimeter Energy Dispersive Spectrometer*

D.E. Newbury, D.A. Wollman (814), K.D. Irwin (814), G.C. Hilton (814), and J.M. Martinis (814)

Objective: Use electron-excited X-Ray spectrometry to determine chemical state.

Problem: Electron-excited X-Ray spectrometry, as performed in the scanning electron microscope and analytical electron microscope, is typically regarded as an elemental analysis method. However, characteristic X-Ray photons with energies less than approximately 1 keV are created as a result of electronic transitions involving the outer shell electrons that are also involved in chemical bonding. Careful examination of X-Ray spectra recorded with high spectral resolution, wavelength dispersive spectrometry (WDS, $\Delta E \approx 2$ to 5 eV) often reveals shifts in the position of low energy characteristic X-Ray peaks as well as changes in the peak shape that can be correlated with the chemical state. While such chemical information is quite valuable for comprehensive characterization, chemical state studies are rarely performed with WDS because of the significant time penalty incurred due to the relatively low geometric and quantum efficiencies of WDS and the requirement for time serial scanning. The inefficiency of WDS necessitates the use of high beam currents (100 nA or more) for peak scans in a reasonable amount of time (1000 s). For radiation sensitive materials, this may mean that the material undergoes alteration while the peak is being scanned, rendering interpretation difficult if not meaningless.

Approach: The new NIST Microcalorimeter Energy Dispersive X-Ray Spectrometer brings important new capabilities that will enable chemical state studies to be performed on a more routine basis. Most important is the resolution performance. In the year since initial publication of the microcalorimeter characteristics, a critical advance has been made in the resolution performance, from $\Delta E = 8$ eV to $\Delta E = 3.1$ eV, full peak width at half maximum (FWHM). At a resolution of 3.1 eV FWHM, the microcalorimeter EDS performance is comparable to that achieved with the best diffraction crystals used in WDS on electron probe microanalyzers (TAP for the photon range from 500 eV to 2.5 keV), and is actually superior to the performance of the synthetic multilayer diffractors ($\Delta E \approx 10$ eV) now favored for the low energy range from 100 eV to 500 eV. The microcalorimeter energy dispersive operation means that the full peak is measured simultaneously, so that time dependent radiation effects can be studied.

Results and Future Plans: The figure shows similar peak shifts and shape changes measured with the microcalorimeter EDS and WDS for Fe L-shell X-Rays from iron metal and hydrated iron oxide. While equivalent results are found, the microcalorimeter can obtain the measurement with lower electron dose. Further improvement in resolution may be possible with the development of a microcalorimeter dedicated exclusively to the photon energy range from 100 eV to 2 keV, which also defines the range of interest for chemical effects.

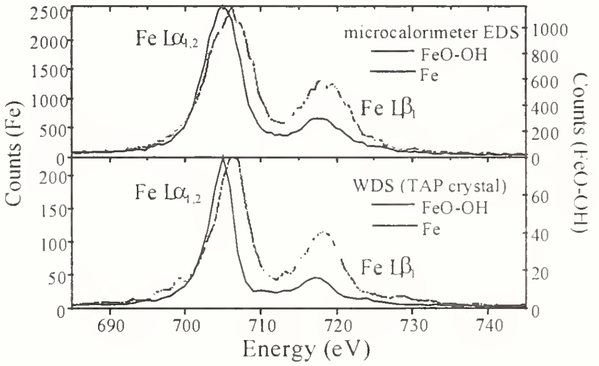


Figure 1. Spectral shifts for iron L-shell X-Rays with WDS and NIST microcalorimeter spectrometer.

2. *Evaluation of Calculated and Measured Electron Inelastic Mean Free Paths near Solid Surfaces*

C.J. Powell and A. Jablonski (Institute of Physical Chemistry, Warsaw)

Objective: To provide evaluated electron inelastic mean free path (IMFP) data for applications in surface analysis.

Problem: The IMFP is a key parameter in the widely-used surface-analysis techniques of Auger-electron spectroscopy (AES) and X-Ray photoelectron spectroscopy (XPS). The favorable surface sensitivity of AES and XPS arises largely from the fact that the IMFP is typically between about 3 Å to 50 Å for electron energies between about 50 and 2,500 eV, the range of practical interest for these techniques. The IMFP is also needed for making matrix corrections in quantitative surface analyses by AES and XPS and in calculations of the transport of the signal electrons in AES and XPS for different purposes.

Approach: IMFPs can be both calculated and measured but it has been difficult to obtain reliable data. Briefly, a number of approximations have been made in the calculations but the magnitudes of the resulting systematic uncertainties have only been estimated. The experimental measurements are subject to other uncertainties that have also only been estimated. In addition, there has been a conceptual difficulty in that the IMFP has been defined and calculated for bulk solids whereas the measurements have been made in the vicinity of surfaces. For example, some recent calculations have indicated that the effective IMFP near surfaces could be up to about 50 % larger than the corresponding bulk IMFPs.

An analysis has been made of the consistency of calculated and measured IMFPs. Seven elemental solids were identified (Al, Si, Ni, Cu, Ge, Ag, and Au) for which there were calculated IMFPs from at least two sources and measured IMFPs from at least two sources. The IMFP measurements were made with the relatively new technique of elastic-peak electron spectroscopy and most of the calculated IMFPs were derived from experimental optical data. A detailed examination was made of the sources and likely magnitudes of uncertainty in the IMFP calculations and measurements.

Results and Future Plans: The calculated IMFPs for Al, Ni, Cu, Ag, and Au from different groups showed a high degree of consistency. For the group of seven elements, the average value of the root-mean-square deviations of the calculated IMFPs from a function fitted to all of the calculated IMFPs for each element was 0.89 Å, and the average mean percentage deviation was 4.4 %. The measured IMFPs for Cu and Ag from different laboratories showed reasonable consistency. For the group of seven elements, the average value of the root-mean-square deviations of the measured IMFPs from a function fitted to all of the measured IMFPs for each element was 3.00 Å, and the average mean percentage deviation was 13.2 %. The measured IMFPs for Ni, Cu, Ag, and Au showed good consistency with the corresponding calculated IMFPs. For the group of seven elements, the average value of the root-mean-square deviations of the measured IMFPs from the function fitted to all of the calculated IMFPs for each element was 4.56 Å, and the average mean percentage deviation was 17.4 %. The same four elements (Ni, Cu, Ag, and Au) showed the greatest overall consistency in their calculated IMFPs, in their measured IMFPs, and between their measured and calculated IMFPs. IMFPs for these materials, determined for electron energies between 50 eV and 10^4 eV, are recommended for use as reference IMFPs in the new NIST Electron Inelastic-Mean-Free-Path Database (SRD 71). There was no clear experimental evidence for a surface correction to calculated IMFPs for bulk solids although the effect of surface roughness in the IMFP measurements needs to be determined. A series of IMFP measurements is planned at NIST with a new AES instrument now being procured. Comparisons will be made of IMFPs measured by three independent methods.

Publication:

Powell, C. J., and Jablonski, A., ***"Evaluation of Calculated and Measured Electron Inelastic Mean Free Paths Surfaces,"*** J. Phys. Chem. Ref. Data (submitted).

3. *Quantifying the Non-Fossil Fraction of Volatile Organic Compounds in Ozone Production in the Los Angeles Basin*

G.A. Klouda and C.W. Lewis (U.S. EPA)

Objective: To provide unique measurements for a current assessment of the non-fossil portion of volatile organic compounds (VOC) that contribute to tropospheric ozone production in the Los Angeles Air Basin.

Problem: Many regions throughout the United States have difficulty complying with the National Ambient Air Quality Standard (NAAQS) for ozone concentration. This air quality standard has recently been lowered to 80 ppbv, averaged over 8 hours, making compliance problematic. Atmospheric non-methane VOC play an important role in ozone formation when combined with nitrogen oxides and sunlight. Radiocarbon (^{14}C) measurements of VOC fractions are valuable in identifying the origin of constituent compounds. ^{14}C is absent in fossil fuels (auto emissions) yet present in non-fossil living materials, *e.g.*, vegetative and charbroiling emissions. at measurable levels, $^{14}C/^{12}C \approx 1.2x10^{-12}$, and both source types contribute to atmospheric VOC.. By measuring the ^{14}C abundance of atmospheric VOC, the portion of non-fossil and fossil VOC can be accurately estimated. Consideration of carbon isotope measurements of the VOC fraction, its chemical composition, and meteorological information is expected to lead to more accurate estimates of the controllable emission sources. With a better understanding of sources and their contributions, more effective strategies can be implemented to control ozone concentrations.

Approach and Results: Air samples (0.1 m^3) were collected during September 1997 at the Azusa, CA air monitoring station during the periods covering 0600-0900, 1300-1600, and 1700-2000 h. Samples were subsequently processed to recover the VOC fraction for ^{14}C measurements. Also, samples of whole gasoline and local vegetation, representative of fossil fuel- and biomass sources of VOC, were collected and prepared for ^{14}C measurement. The results of the gasoline, vegetation, and CO_2 separated from whole air were consistent with the lack of ^{14}C in gasoline and contemporary living material. These measurements are necessary input to the ^{14}C (two-source) model used to deter-mine the portion of non-fossil VOC. The atmospheric VOC concentrations ranged from 358 nmol to 710 nmol C mol^{-1}. Based on the VOC fraction ^{14}C results and the source materials (living and dead), the VOC percentage originating from non-fossil fuel sources during these periods ranged from 4 % to 48 % with an average of 23 %. The general trend observed was one of decreasing non-fossil percentage with increasing VOC carbon concentration (see Figure 1). This is consistent with high pollution events driven more by fossil fuel than by non-fossil related emissions.

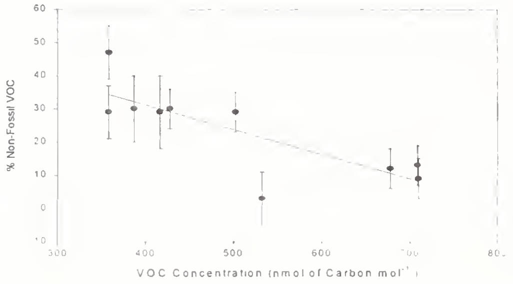


Figure 1.Non-fossil VOC fraction as function of VOC concentration.

Future Plans: ^{14}C-VOC measurements on samples collected in Houston, TX, and Nashville, TN will be completed using the same methodology. A new sampling approach to improve the overall precision of the results by collecting VOC from 1 m^3 to 10 m^3 of air will enhance the analytical signal for chemical and isotopic measurements, lower the chemical blank, and provide better estimates of non-fossil VOC emissions. It has been tested at NIST (MD) and Duke Forest (NC) and is planned for deployment in Nashville, TN in conjunction with the Southern Oxidants Study (SOS) Field Intensive in June of 1999. The new method will also provide a field separation of hydrocarbons from oxygenated-hydrocarbons for separate ^{14}C measurement and $\delta^{13}C$ measurements of individual VOC compounds. The added resolution in the chemical and isotopic patterns of VOC is expected to lead to a better understanding of the complex atmospheric chemistry involved in ozone formation.

4. *Radiocarbon Measurements in Support of the Northern Front Range Air Quality Study*

***D.B. Klinedinst** and L.A. Currie*

Objective: To provide definitive discrimination and quantification of fossil and modern (biomass) carbonaceous atmospheric aerosols along the Northern Front Range of Colorado.

Problem: The Denver "Brown Cloud" is a well-known and extensively studied wintertime air pollution phenomenon. Over the past three decades, air quality along the Northern Front Range of Colorado has improved. In fact, during the past two winters there have been no violations of Federal ambient air quality standards, including the $PM_{2.5}$ air particulate standard promulgated by the U.S. EPA in 1997. However, the State visibility standard for the Denver metropolitan area continues to be frequently violated year round. In 1995, in response to continuing public and political concerns, the General Assembly of the State of Colorado enacted House Bill 1345, which established the Northern Front Range Air Quality Study (NFRAQS). The legislation called for an "independent, objective, scientifically peer-reviewed study" to identify and apportion sources of pollution along the Northern Front Range that contribute to Denver urban visibility degradation. The study focused on $PM_{2.5}$ pollution and its precursors.

Approach: A significant portion of the $PM_{2.5}$ mass in the Denver area on high pollution, low visibility days consists of carbonaceous aerosols. Radiocarbon (^{14}C) analyses of selected ambient and source samples from the NFRAQS domain were performed by NIST to provide a direct, assumption-free measure of the fossil *vs.* biomass carbon fractions. The ^{14}C analysis of atmospheric aerosol is reported as the fraction of modern carbon (f_M), which is ^{14}C activity of a sample relative to the bomb-corrected ^{14}C activity of the modern oxalic acid radiocarbon standard (SRM 4990B) and thus, *by definition,* apportions the carbon fraction into its fossil and biomass components. Over 100 ^{14}C analyses of the total non-carbonate carbon fraction of both ambient and source $PM_{2.5}$ samples were made. The winter ambient samples were collected in Denver at the Welby and Brighton core sites and consisted of sixteen simultaneously collected pairs. The suite of source samples, collected in Denver during the study period consisted of $PM_{2.5}$ particulate emissions derived from hard and soft woods, synthetic logs, meat cooking, summer and winter light duty vehicles, heavy duty diesel trucks and $PM_{2.5}$ size segregated road dust. Sample carbon was measured *via* accelerator mass spectrometry (AMS) using sample preparation methodologies developed in our laboratory for very small samples i.e., <100 μg C (Verkouteren, Klinedinst and Currie, 1997). AMS measurements were made at the University of Arizona–NSF AMS Facility.

Results and Future Plans: For the sampling days and periods analyzed for ^{14}C, the predominant ^{14}C signature in both the summer and the winter was fossil carbon. Source samples analyzed for ^{14}C were consistent with fossil- (petroleum derived) or biomass-derived carbon expectations. The apportionment of carbonaceous aerosol for the NFRAQS study was performed using a chemical mass balance (CMB) source-receptor model (Watson, et al., 1998). It is well known that CMB carbon source apportionment can be extremely sensitive to the source profile model input. The radiocarbon analyses were, therefore, of extreme importance to the study in that they served as an independent, direct measure of the fossil vs. biomass apportionment and provided a rigorous constraint on the CMB model output. This, in turn, lead to a policy-relevant conclusion that, with few exceptions, vehicular sources are the primary contributors to $PM_{2.5}$ carbon in Denver during both the summer and the winter.

Publications:

Verkouteren, R.M.; Klinedinst, D.B.; and Currie, L.A. (1997) "**Iron Manganese System for Preparation of AMS Targets: Characterization of the Chemical-Isotopic Blanks and Fractionations**" Radiocarbon, 39, 269-283.

Watson, J.G., Fujita, E.M., Chow, J.C., Zielinska, B., Richards, L.W., Neff, W., Dietrich, D., (1998) **"Northern Front Range Air Quality Study Final Report"** Desert Research Institute Document N. 6580-685-8750-IF2, Reno, NV.

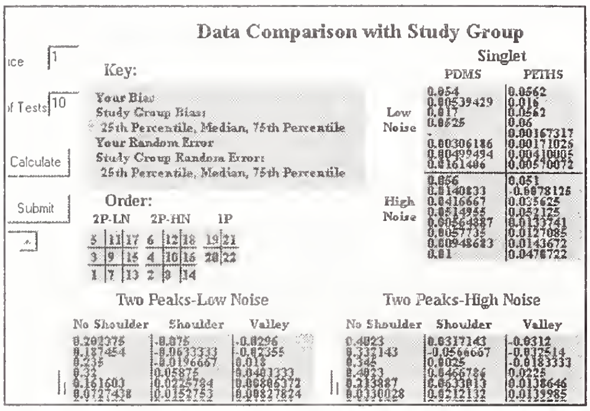
5. *Interactive Standard Test Data: Evaluating Performance of Instrument Data Analysis Procedures on the Web*

J.M. Conny and J.N. Lee

Objective: Provide Interactive Standard Test Data as a web-based service (www.acg.nist.gov/std/) to allow users to evaluate computer-based data analysis procedures associated with analytical instrumentation such as smoothing, baseline correction, and curve fitting.

Problem: Data analysis software associated with instrumentation commonly allows users to choose from a number of analysis options. Many analysts employ the 'default' analysis procedures, and as a result are unaware of the extent that different procedures cause error. For instrumental methods that produce responses as peaks, error should be quantified for peak parameters such as position and area. For this purpose, we provide test data with well-characterized peak parameters, which users may determine with software procedures of their choice. However, along with dissemination of the test data, a mechanism is necessary for evaluating an analyst's estimates of the peak parameters from the test data, and for the analyst to compare his/her data evaluation with those of other analysts.

Approach: X-Ray photoelectron spectra (XPS) were simulated by fitting spline functions to measured spectra, resulting in peak parameters that are defined mathematically rather than estimated. Following a factorial design, the standard test data (XPS-STD) consist primarily of polymer carbon 1s doublet spectra that present varying degrees of overlap between peaks, varying levels of relative intensity between peaks, and varying levels of Poisson noise. Non-linear least-squares fits of the XPS-STD by 20 analysts using a variety of software procedures revealed peak binding energies (locations) and intensities (areas) that deviated substantially from the true binding energies and intensities. These deviations from the true values, calculated as biases and random errors, are the evaluated results of the Study Group. Users first download the XPS-STD from the web site and use their own software to analyze the spectra for peak binding energies and intensities. Then, users upload their results back to the web site for an on-line evaluation of their results. Users may compare the on-line evaluation of their results with that of the Study Group. In addition to on-line evaluation of data analysis results, the web site is a database that acquires the biases and random errors along with the type of data analysis procedures employed. By minimizing biases and random errors in the evaluated results for a particular spectral condition modeled by the XPS-STD, users may determine which analysis procedures produce high accuracy and precision.



Data Comparison with Study Group

Key:

- Your Bias
- Study Group Bias:
  - 25th Percentile, Median, 75th Percentile
- Your Random Error
- Study Group Random Error:
  - 25th Percentile, Median, 75th Percentile

Order:

2P-LN			2P-HN			1P	
5	11	17	6	12	18	19	21
3	9	15	4	10	16	20	22
1	7	13	2	8	14		

Singlet

	PDMS	PETHS
Low Noise	0.054 0.00539429 0.017 0.0525 - 0.00306186 0.00499494 0.0161486	0.0562 0.016 0.0562 0.06 0.00167317 0.00171025 0.00410005 0.00570072
High Noise	0.056 0.0140833 0.0416667 0.0514955 0.00564887 0.0057735 0.00948683 0.01	0.051 -0.0078125 0.035625 0.052125 0.0133741 0.0127085 0.0143672 0.0478722

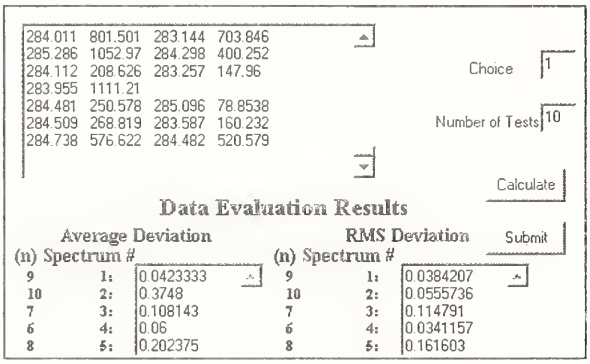
Two Peaks-Low Noise

No Shoulder	Shoulder	Valley
0.202375	-0.075	-0.0296
0.187454	-0.0633333	-0.02355
0.235	-0.0196667	0.018
0.32	0.05875	0.0403333
0.161603	0.0225784	0.00806372
0.0727438	0.0152753	0.00827824

Two Peaks-High Noise

No Shoulder	Shoulder	Valley
0.4023	0.0317143	-0.0312
0.332143	-0.0566667	-0.017514
0.345	0.0025	-0.0183333
0.4023	0.0466786	0.0225
0.213887	0.0633013	0.0138646
0.0330028	0.0212132	0.0139985

Results and Future Plans: Biases in peak binding energies for the Study Group ranged from -0.055 eV to 0.34 eV, while random errors ranged from 0.012 eV to 0.13 eV. Results indicated that data analysis of doublet spectra may be problematic, since up to 50 % of the XPS-STD doublets were incorrectly assigned as singlets. The figures show sections of the web page that display the evaluation of binding-energy data. Users paste their binding-energy and intensity data to the upper left window (upper figure), indicate the number and index of spectra sets analyzed, and then push Calculate. Various tables appear with statistics as biases and random errors for the different spectra conditions for the user and the Study Group (lower figure). Database information will guide future Interactive Standard Test Data products.



```
284.011  801.501  283.144  703.846
285.286  1052.97  284.298  400.252
284.112  208.626  283.257  147.96
283.955  1111.21
284.481  250.578  285.096  78.8538
284.509  268.819  283.587  160.232
284.738  576.622  284.482  520.579
```

Choice 1

Number of Tests 10

Data Evaluation Results

(n)	Spectrum #	Average Deviation	(n)	Spectrum #	RMS Deviation
9	1:	0.0423333	9	1:	0.0384207
10	2:	0.3748	10	2:	0.0555736
7	3:	0.108143	7	3:	0.114791
6	4:	0.06	6	4:	0.0341157
8	5:	0.202375	8	5:	0.161603

6. Internal Isotopic Consistency in Isotope Ratio Mass Spectrometry: A New Paradigm for Achieving Accurate Measurements with Molecular Ions

R.M. Verkouteren

Objective. To assign precise and accurate values to isotopic Reference Materials by verifying the accuracy of differential isotope ratio measurements through the comparison of calculated and observed ratios in the extended spectra of molecular ions.

Problem: The isotope ratio (r) in a sample, measured relative to the isotope ratio (R) in a reference material, is the time honored method for reporting an isotopic composition, where $\delta = 1000(r-R)/R$ and *delta* is expressed in *per mill* (‰). Although the reporting of ratios between measured ratios would seem to compensate for instrumental factors, the reproducibility of isotopic measurements across laboratories can be ten times poorer than the analytical repeatability achievable in modern isotope ratio mass spectrometers. A recent comparison exercise organized here for the value assignment of CO_2 isotopic Reference Materials (RMs 8562-8564) showed that interlaboratory reproducibility degraded as the difference (r–R) increased. This effect was attributed to "cross contamination" between the sample and Reference Material, and was due to a variety of small but significant sorption and outgassing effects in the ion source. Because every mass spectrometer is unique in history of use, cleanliness, filament age, source design, and conductance characteristics, cross contamination levels vary. As a result, measurements where $r-R \neq 0$ are prone to biases that can be up to 1 ‰ for typical samples. Until this time no method was available to ascertain the accuracy of any particular determination, and RM value assignment was problematical.

Approach: Carbon is essentially ^{12}C (≈98.9 %) and ^{13}C (≈1.1 %), and oxygen is ^{16}O (≈99.8 %), ^{17}O (≈0.04 %), and ^{18}O (≈0.2 %). Natural CO_2 is therefore comprised of masses 44 through 49 in abundances predictable by the isotopic abundances of the constituent carbon and oxygen atoms. In typical CO_2 isotope ratio mass spectrometry, two ratios are measured: mass 45 to mass 44 (for $\delta^{45}CO_2$), and mass 46 to mass 44 (for $\delta^{46}CO_2$). The $\delta^{45}CO_2$ and $\delta^{46}CO_2$ measurements have the information sufficient to calculate carbon and oxygen isotopic compositions relative to reference CO_2, but without verification of accuracy.

With Finnigan (Thermoquest Corporation), we tested new ion source components designed to minimize cross contamination, and extend capabilities of the faraday cup detector array to allow the additional CO_2 ion ratio measurement of mass 47 to mass 44 (for $\delta^{47}CO_2$). This measurement, originally considered to be redundant, will allow verification of $\delta^{45}CO_2$ and $\delta^{46}CO_2$ measurement accuracy by comparing the measured value of $\delta^{47}CO_2$ with that calculated (hence expected) from accurate $\delta^{45}CO_2$ and $\delta^{46}CO_2$ measurements. Cross contamination, along with other instrumental effects and isobaric contamination, results in a divergence of the measured and expected values of $\delta^{47}CO_2$. Statistical equality between the measured and expected values is, therefore, a necessary condition of measurement accuracy, and a new paradigm for the accurate isotopic measurement of many molecular species.

Results and Future Plans: Measurements of $\delta^{45}CO_2$, $\delta^{46}CO_2$ and $\delta^{47}CO_2$ were made between two CO_2 materials (purity > 99.995 %) differing significantly in carbon and oxygen isotopic compositions. A series of measurement protocols were used that varied the degree of cross contamination in the ion source. Measured and expected values of $\delta^{47}CO_2$ were then plotted *versus* changes in the measurement protocols, and compared in value and sensitivity to the protocol. Results indicated that very atypical measurement protocols, even with the modified NIST ion source, were necessary to achieve robust statistical equality between the measured and expected values of $\delta^{47}CO_2$. These atypical protocols included an open source design, two minutes of crossover equilibration time (rather than 15 seconds), and inlet gas pressures ten times greater than usual. When these same protocols were applied to the measurement of the isotopic RMs 8563-8564 and compared to the measurements taken during the comparison exercise, clear and reasonable patterns emerged that allowed precise and accurate value assignments for these RMs. A new comparison exercise is now being organized, designed to compensate for variations in cross contamination, that will provide definitive consensus values for these and other key isotopic RMs.

7. *Nature and Distribution of the Blank: Impact on Low-Level and High Accuracy Chemical Metrology*

L.A. Currie, G.A. Klouda, and D.B. Klinedinst

Objective: To determine the fundamental nature of the blank and its impact on *both* low-level and high accuracy isotopic-chemical metrology, with special significance for selected industrial and other agency cooperative programs.

Problem: The distribution of the blank is the single, most important factor influencing detection capabilities for low-level measurements. Erroneous assumptions concerning variance or form of the blank distribution function can therefore have a profound effect on the validity of presumed detection and quantification limits. Similarly, in high accuracy metrology, the variability of the blank may have an over-riding effect when other uncertainty components are quite small. Opportunities to investigate both metrological poles of blank influence arose in:

1. a high-accuracy dual isotopic "fingerprinting" cooperative program, where extremes of precision were needed to discriminate among chemically identical industrial feedstocks or manufactured products and
2. a low-level atmospheric radioactivity program for another agency, where it was urgent to transcend the state-of-the-art for detecting minute amounts of atmospheric source and transport tracers.

In the first case it was necessary to determine the bivariate. ^{13}C-^{14}C character of the blank, to quantify its influence on the high precision confidence regions for the industrial materials. In the second, it was essential to test the validity of the commonly assumed, but not necessarily correct, Poisson distribution for low-level background radiation.

Approach: The key to assessing the limitations of the blank on the high accuracy isotopic fingerprinting study lay in the development of new methods for ultra-low-level measurements of blanks by "dilution accelerator mass spectrometry," which allows us to measure natural ^{14}C in just a few µg carbon. This is essential because the blank accounts for about 1 % of the sample, yet the latter can be measured with u_i<0.3 %. In the second study, the key to developing the most powerful test for the validity of the Poisson hypothesis for low-level (anticoincidence [AC]) background radiation is the unique NIST individual pulse analysis system[1]. The ability to capture the entire (10-day) history of a 300,000 pulse data stream with 1 µs resolution makes it possible to test the independence of background events, the uniform distribution of arrival times, and the exponential distribution of inter-arrival times. Such tests are far more sensitive than the conventional approach, which examines the Poisson distribution of counts. Such multi-distributional analysis has the potential to reveal several different types of artifacts, and it has the special advantage of utilizing all of the information from a single extended measurement period, rather than requiring many replicates of such extended periods.

Results: For the industrial study, the ability to measure µg levels of ^{14}C in the isotopic fingerprinting blank has been crucial in achieving the inherent (0.3 %) u_i capability for mg amounts of the industrial materials. Uncertainty in the isotopic composition of the blank previously led to an inflation of u_c by nearly an order of magnitude, thus limiting the excellent isotopic discrimination capabilities for industrially-important materials. In the second study, evaluation of the counts and arrival times showed no detectable deviation from the Poisson hypothesis for the net (AC) background, but for the extended time series it did show extra variance for the gross background that could be linked to the barometric pressure. This is important, because in the absence of AC the independence criterion for random events is violated. More crucial, for low-level (AC) counting, were very significant interactions between AC and coincidence (mu meson) events, that gave rise to an 8 % rate of spurious background counts (afterpulses). This could not have been detected without the ability to study the inter-arrival times for the two classes of events.

Publication:

Currie, L.A., Eijgenhuijsen, E.M., and Klouda, G.A., "***On the Validity of the Poisson Hypothesis for Low-Level Counting: Investigation of the Distribution Characteristics of Background Radiation with the NIST Individual Pulse Counting System***," Radiocarbon 40 (1998) 113-127.

8. Fractal Dimension of Particle Outlines: Meaning, Limitations, and Use

D.S. Bright

Objective: To implement a method for measuring the fractal dimensions of particles (D), characterize it, and relate it to more commonly used measurements and obvious visual characteristics of the outlines of particles and grains observed in microscope images.

Problem: Shapes of particles are often complex and difficult to characterize. Only a handful of basic shape measurements are in common use, e.g., length, width, and perimeter. Other less used shape parameters include distance map maximum, mean curvature, and principal axes. The goal is to characterize one or two methods for measuring D from digitized images, and assess the utility of D as another basic shape measurement. Will D distinguish roughness and large shape features? Since no particle outline is truly a fractal, how can one determine a size range for a valid or useful value for D? How is the D measurement affected by touching particles, over-all particle shape, incomplete boundaries, microscope resolution, and noise?

Approach: From about a dozen methods that have been reported for measuring the fractal dimension of outlines, I chose two that were recommended in the literature: the Serpinski Sausage (SS) method that uses the Euclidian Distance Map of an image, and the Coordinate averaged Richardson plot. Unlike previous studies that tested measurement methods with a few mathematically generated fractals of known D, this work uses a family of fractals with a continuum of available D values with a variety of shapes for each D (Figure 1a-d). (These figures alone indicate what sort of families of outlines will not be distinguishable by D measurement.) I added tools to MacLispix to generate curves, measurements and plots. D is measured as the slope of a log-log plot of perimeter vs. step size where fractal behavior gives a straight plot. Figure 1e, a plot for fractal 1a, is slightly curved – plots for real particles are often curved more than this. The questions are:

- which section of the plot gives the best value for D? and
- how much curvature indicates non-fractal behavior or a non-useable D?

These are being investigated. Also, obviously non-fractal shapes that do give linear plots have been encountered. What does all this imply for the utility of D values?

Results and Future Plans: The two methods of measuring D have limitations both in the range of D and in the shape parameter, this may reflect limitations of digitization as well as of each method. Despite the limited step size range over which D might be valid, the curvature of the plot within this range, and the circumstantial linearity for non-fractal shapes, a preliminary investigation used D values to discriminate between four different tree leaf shapes (scanned directly on scanner, 5-10 leaves per group). I am now collecting electron micrograph images of soil particles for a more extensive and realistic test.

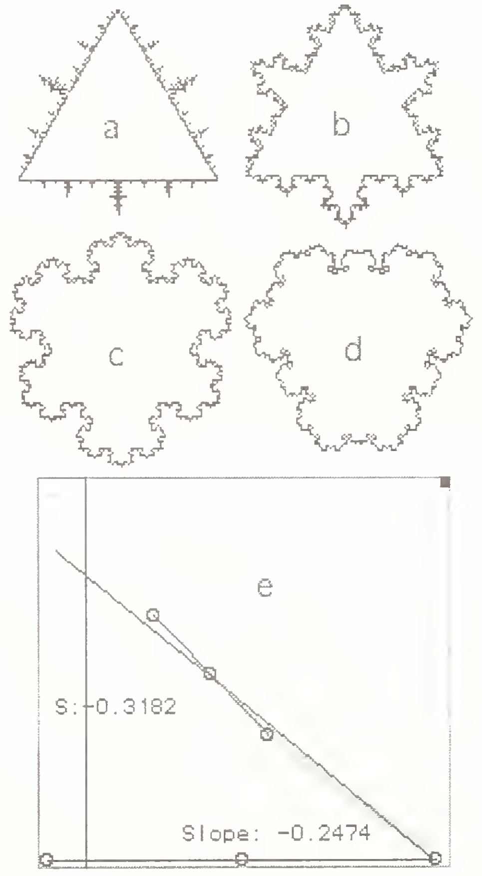


Figure 1. a-d: sample test fractals, all with nominal D=1.3. Measured D (1-slope, SS method) a=1.247, b=1.306, c=1.303, d=1.258. e: plot for a, SS method. Note slight curvature, range of slopes.

9. *Grazing Incidence X-Ray Photoemission Spectroscopy for Measuring Semiconductor Oxide Layers*

T.J. Jach

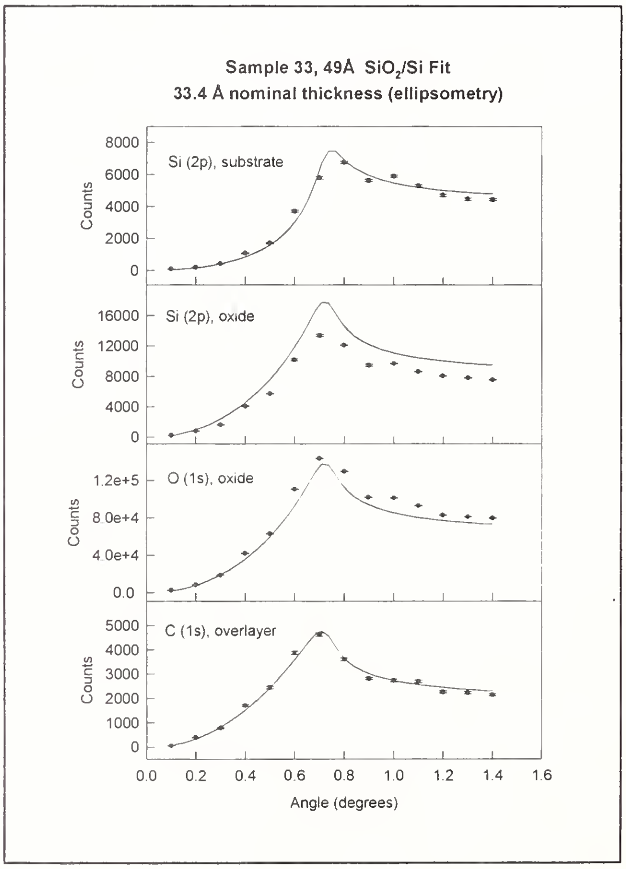
Objective: To develop a technique suitable for measuring the chemical state, constituents, thicknesses, and densities of oxide layers of thickness less than 10 nm on semiconductor substrates.

Problem: The SEMATECH roadmap anticipates the need for device gates with oxide thicknesses of less than 10 nm. The semiconductor industry is wedded to traditional non-destructive measurement methods (ellipsometry) that are calibrated for much thicker oxides. Other methods, which can be used to calibrate the procedures for the measurements of thinner oxides (e.g. secondary ion mass spectroscopy, transmission electron microscope cross-sections, X-Ray reflectivity), all have some aspect that equally needs validation in the case of oxides with thicknesses below 100 nm. In addition, these methods do not readily provide information on the chemical state of the insulating species.

The current trend in the semiconductor industry is towards complex gate oxides that contain extra species (for example, nitrogen) at the interface with the substrate. With current techniques, it is not possible to determine non-destructively the chemical state and the depth of these complex oxides.

Approach: While some use of X-Ray photoemission spectroscopy employs larger or smaller angles of incidence to separate the effects of oxide from the substrate, no attempt is normally made to take advantage of the fact that the index of refraction at X-Ray energies is different in the oxide and the substrate. The X-Ray fields in the layer(s) and substrate change extensively at very small incidence angles. By taking X-Ray photoemission spectra at a series of grazing angles, and fitting the intensities of the photoemission peaks to the dependence of yields on the physical parameters of the layers, we hope to take advantage of the extra physical information present in the optical properties of the layers at X-Ray energies to determine thickness, composition, and density of the layer(s).

Results and future plans: Earlier implementations of this method were tested out in the laboratory, and the rate of data acquisition was extremely slow. We have set up a system which makes the measurements using a collimated, monochromatic beam of X-Rays on the X-24A beamline at the National Synchrotron Light Source. A sample of the results with fits to a thickness are shown in Figure 1. The photoemission behavior is in good agreement with the theoretical predictions. The fits from several samples indicate precisions of a few angstroms for the layer thicknesses. However the thicknesses are consistently greater than the numbers obtained from conventional ellipsometry used to characterize the samples. Our future plans call for carrying out combined measurements using the various available techniques to understand inconsistencies between the measurements.



10. An Electron Probe Microanalysis Study of Tungsten Carbide–Cobalt Powders for Coatings

R.B. Marinenko *and E.B. Steel*

Objective: The objective is to characterize on the micrometer scale tungsten carbide-cobalt powders from different manufacturers and preparation procedures and to determine how the Co was distributed in the tungsten carbide (WC) phases.

Problem: Possibly two out of the five specimens analyzed in this work were candidate materials for development as Standard Reference Materials (SRMs). The NIST Ceramics Division had analyzed these powders using macro techniques such as X-Ray diffraction and optical microscopy. A detailed microanalysis was needed to determine the elemental distributions from particle to particle and within individual powder particles to define clearly the chemical and physical microstructure of these powders.

Approach: Specimens from each of the five powder samples were dispersed onto carbon tape with an air jet which resulted in no or little particle agglomeration. Secondary and backscatter electron images were taken using the electron microprobe to study particle morphology, EDS spectra were taken to evaluate qualitative chemical compositions, and EDS X-Ray digital maps were acquired to determine spatial distributions of C, W, and Co. In addition, an automated particle analysis procedure was later run on three of the five samples, quantitatively analyzing 150-500 particles from each. The automated particle analyses were run to determine if the heterogeneity were consistent throughout each specimen, if it were consistent within large particles (greater than about 10 μm diameter), and if the composition could be related to particle size. Only W and Co were analyzed since the C peak from the acquisition system was not clearly resolved for quantitation. Carbon therefore was determined by difference. For larger particles, several points were analyzed, the number depending upon the particle size.

Results: Based on particle morphology, the samples were divided into two groups. The fused and crushed samples had smaller shard-like particles (a few micrometers to about 30 μm in diameter) while the agglomerated and sintered samples were composed of large (mostly 30 μm to 70 μm diameter), rounded particles, sometimes appearing to be agglomerates of smaller particles. Point beam EDS analysis showed a large variation in the relative element peak intensities for C, Co and W from particle to particle and within those particles that were large enough for multiple analyses. EDS X-Ray element maps confirmed this heterogeneous distribution, particularly for the Co that appears to be independent of the WC phase or phases and is present in a lesser amount, possibly acting as glue between globules of the WC material, e.g., see Fig. 1 taken from a 70 μm particle in an agglomerated/sintered specimen. Data from the automated particle analyses confirmed that there is a considerable range of compositions (at least ±5-10 % relative) for each of the elements and that the heterogeneity within the larger particles can be as great or greater than the heterogeneity between particles. Also, there was no relationship between particle size and composition.

These data demonstrate the importance of microanalysis for a complete understanding of the materials in technology and science. The heterogeneity of the C, W, and Co exists throughout the particles. Future work will include the use of these microanalysis procedures in understanding the structure of these materials after exposure to high temperatures.

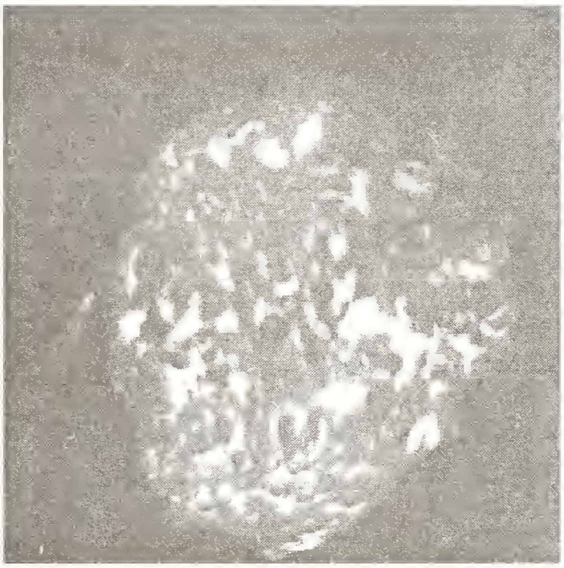


Figure 1. EDS CoK X-Ray map.

11. *Improved Accuracy in Quantitative Electron Beam Analysis of Particles: The Effects of Low Voltage Excitation on Particle Geometry Corrections*

J.A. Small

Objective: To develop a novel approach to the quantitative electron probe analysis of micrometer-sized particles based on low voltage analysis with electron beam energies less than 10 keV.

Problem: In conventional electron probe microanalysis, the energy of the electron beam is generally in the range of 15 keV to 25 keV which provides the necessary overvoltage to excite efficiently the K and L X-Ray lines for elements with atomic numbers (Z's) in the range of about 25 to 83. Historically this same range of beam energies has been applied to the microanalysis of particles. At these beam energies, however, particle size and morphology play a critical role in the generation and emission of X-Rays and can significantly affect quantitative analytical results.

Recent instrumental developments in electron beam microanalysis including the field-emission gun scanning electron microscope, FEG-SEM, and the high-resolution microcalorimeter X-Ray detector will make it possible to use electron beam energies in the range of 5 keV to 10 keV for analysis rather than 15 keV to 25 keV. The lower energy electrons can be used to excite characteristic X-Ray lines with energies less than about 4 keV. Employing the characteristic X-Ray lines, with energies from 0.640 keV to 2.42 keV, for the elements with Z's in range 25-83, rather than the characteristic X-Ray lines with energies 5.85 keV to 10.83 keV, should reduce the effects of particle size and morphology and significantly improve the quantitative results.

Approach: To study the effects of reducing the accelerating voltage on particle analysis, we analyzed irregularly-shaped particles from SRM 470 (K-411 glass) ranging in size from about 1 μm to 24 μm at beam energies of 10, 17, 20, 22, and 25 keV. The shards were analyzed in an electron probe employing energy dispersive X-Ray spectrometry. Quantitative analysis was performed with a conventional bulk-sample correction algorithm that involved the comparison of the X-Ray intensities from the particles to the intensities from bulk standards. Standards included MgO for Mg, SiO_2 for Si, SRM 470 (glass K-412) for Ca, and SRM 470 (glass K-411) for Fe. A Multi-linear-least-squares fitting procedure was used with reference peak shapes for background subtraction. The relative errors for all elements were then calculated for each particle as a function of beam energy.

Results and Future Plans: The results of the analysis are shown in Figure 1 which is a plot of the relative errors observed in the quantitative results for all elements for each voltage. The error distributions in Figure 1 are for quantitative results without any normalization or other corrections for particle effects. The results indicate that for beam energies greater than 20 keV the distribution of errors is large, ranging from a high of + 0.6 to a low of -0.5. In contrast, the range of errors for beam energies less than 20 keV drops dramatically with the smallest errors, ranging from + 0.13 to -0.08, occurring at 10 keV. In the future, we plan to extend the analysis of particles to beam energies ≤ 5 keV, utilizing a high-vacuum microscope, and to develop a low-voltage analysis procedure for the analysis of particles at accuracies approaching those for bulk-polished samples, ≤ 5 % relative.

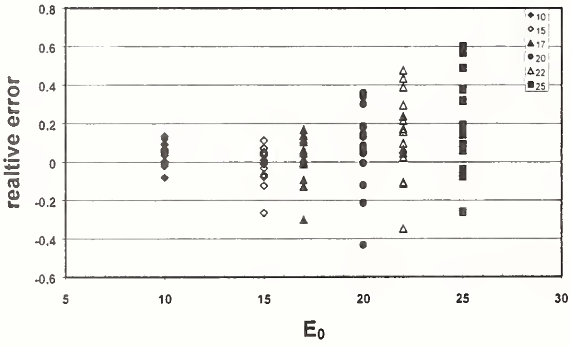


Figure 1. Plot of the relative errors vs. E_0 for the quantitative analysis of glass shards.

12. *Comparing the Electron-Beam Scattering Model for the Environmental Scanning Electron Microscope to Experimental Measurements*

S.A. Wight

Objective: To use experimental measurements to test and improve Monte Carlo models of the electron scattering by gas molecules in the sample chamber of the environmental scanning electron microscope.

Problem: Environmental scanning electron microscopes (ESEM) and the other low vacuum (LV) specimen chamber instruments operate at 133 Pa to 1330 Pa (1-10 Torr). Gas molecules in the specimen chamber neutralize the specimen and eliminate the need for conductive coatings. However, primary electrons are scattered out of the electron beam by gas molecules forming a “skirt” around the point of primary beam interaction with the sample. The “skirt” electrons are capable of generating X-Rays several tens of micrometers away from the primary interaction point. Quantitative data are compromised when these X-Rays reach the detector and are attributed to the material under the primary electron beam. Monte Carlo simulation programs have been developed to predict the scattering of electrons by gas molecules. High quality experimental measurements are needed to improve the Monte Carlo models. An accurate model is important to understand the analytical spatial resolution of energy dispersive spectrometry in an ESEM or LV instrument. Ideally the model generates a correction to analytical data that removes the effect of the scattered electron-generated X-Rays from the spectra.

Approach: A polished copper block was embedded in epoxy, and mounted on the ESEM stage. We collected X-Ray spectra across the epoxy-copper interface by moving the sample in discrete steps under the stationary electron beam. Copper K-alpha X-Ray intensities were determined from the spectra and plotted as a function of distance from the copper-epoxy interface. The spectra were collected at 20 kV accelerating voltage and 266 Pa (2 Torr) water vapor. Next, with the electron beam positioned on the epoxy, 20 µm from the interface, the gas pressure in the chamber was varied. Copper K-alpha X-Rays generated by electrons scattered 20 µm or greater, were measured and plotted as a percentage of the X-Ray counts detected when the beam is on the copper edge of the interface. The Monte Carlo simulations of electron scattering were calculated for the same conditions as the experiments.

Results and Future Plans: The results presented in Figures 1 and 2 show a comparison between experiment and Monte Carlo model. In Figure 1, the Monte Carlo model and the experimental results agree within about 2 %. In Figure 2 the model and the experimental results differ by as much as 10 %. These results indicate that, for this sample, the Monte Carlo model does a reasonable job of modeling the beam spread at a fixed chamber pressure of 266 Pa but not the variation of beam spread with chamber pressure at a fixed distance. In the future, experimental measurements will be made on other systems and the results used to modify the Monte Carlo model.

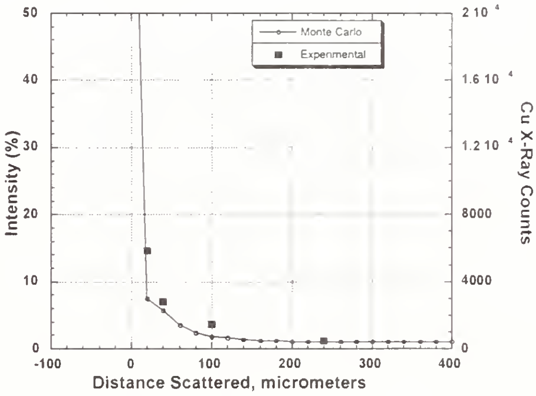


Figure 1. Distance Experiment

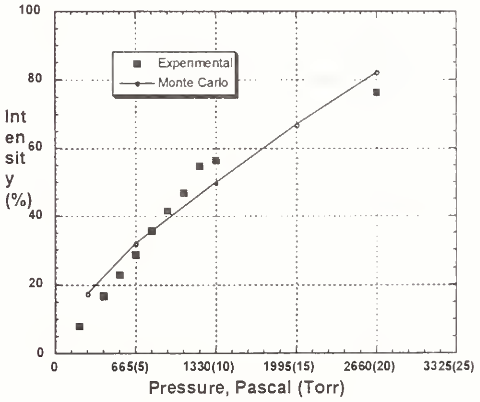


Figure 2. Pressure Experiment

13. *Development of a Novel Approach to Vibrationally Resonant Sum-Frequency Generation*

*L.J. **Richter**, T.P. Petralli-Mallow (831), and J.C. Stephenson (844)*

Objective: To develop a simple, robust approach to the acquisition of vibrationally resonant sum-frequency generation (SFG) spectra, for the *in-situ* study of chemistry at interfaces.

Problem: The molecular structure of interfaces and the chemical reactions that occur at them are critical to industries as diverse as chemical processing, biosensing, and semiconductor electronics. The study of interfaces is difficult as the probe must be both sensitive and selective (discriminate against the bulk material). The nonlinear optical technique of vibrationally resonant SFG has been demonstrated to be a powerful probe of buried interfaces, such as the solid-liquid or liquid-liquid interface, where standard, linear, infrared absorption-spectroscopy is usually impossible. However, SFG has proven to be difficult to implement, as it traditionally involves tuning a custom-built, narrow-bandwidth IR laser through the molecular resonances of interest.

Approach: A commercial, ultrafast, amplified Ti-sapphire pumped optical parametric amplifier is used to generate tunable broad-bandwidth (250 cm^{-1} FWHM) signal (1100 nm-1600 nm) and idler (1600 nm-2600 nm) pulses. Difference frequency generation between these pulses produces broad-bandwidth IR pulses tunable from 2.5 µm to 12 µm. SFG is generated at the interface by mixing these IR pulses with narrow-bandwidth 800 nm pulses derived from the amplified Ti-sapphire pump. The resultant sum frequency light is dispersed by a spectrograph and detected with a research grade CCD camera with 1100 spectral elements. Typically, data over a 500 cm^{-1} spectral region is obtained without tuning the IR source.

Results and Future Plans: Shown in Figure 1 are the dispersed SFG light collected from Au films covered with one monolayer of (a) fully deuterated octadecane thiol (d-ODT) and (b) fully hydrogenated octadecane thiol (ODT). The ratio of (b) to (a) is shown as (c). Each trace represents 60 s of data acquisition. The three strong, sharp features can be assigned to resonances of the terminal methyl group of the ODT. Due to the high degree of order in the film, the methylene group resonances are very weak. Relative to SFG spectra reported in the literature acquired with traditional techniques, the spectra taken with our new method are of superior quality and require much less data acquisition time.

This approach to vibrationally-resonant SFG will be used in the future to perform studies *in-situ* of the molecular conformation and chemistry of hybrid bilayer membranes (HBMs are biomimetic membranes developed by Div. 831) and for the study of the structure and dynamics of active membrane molecules, such as ubiquinone and proteins, in the HBM's. Because our SFG technique offers femtosecond time resolution and complete spectral coverage on every laser shot, it is particularly useful for time resolved studies of molecular dynamics at interfaces (e.g., following a laser-induced change in temperature or pH), and in the study of phase transitions of films induced by changes in surface pressure or temperature.

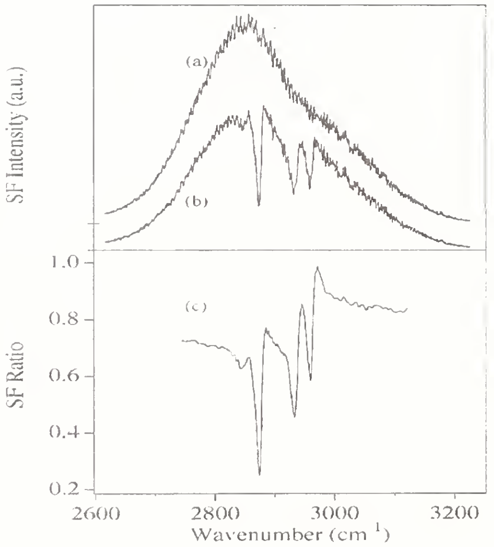


Figure 1. SFG spectrum of a Au film covered with (a) d-ODT and (b) ODT and (c) the ratio (b)/(a).

Publications:

Richter, L.J., Petralli-Mallow, T.P., and Stephenson, J.C., "***Vibrationally Resolved Sum-Frequency Generation with Broad-Bandwidth Infrared Pulses***," Opt. Lett. 23, 1594 (1998).

14. *Information on Surface Dynamics of Dry Etching From Atomic Force Microscopy*

***S.W. Robey** and K. Sinnah (Calvin College)*

Objective: The goal is to develop scanned probe microscopies, in particular atomic force microscopy, to provide information on the surface dynamics leading to roughening during important technological processes such as plasma or wet chemical etching, sputter etching, or thin-film deposition.

Background: Surface processing techniques are employed in a wide range of technologies for surface cleaning, thin-film deposition, and etching. In many cases a premium is placed on reduction in the degree of roughening that occurs during this processing. This makes it imperative to understand the factors leading to the development of surface morphology during thin-film deposition or etching. Extensive work has been performed examining the development of surface morphology, particularly for thin film homoepitaxy, but the vast majority of that work has been couched in terms of thermodynamic models that are applicable when local equilibrium exists. The technological push to lower temperatures to minimize chemical interaction and higher deposition and etching rates for production economy push surface processing far into kinetically limited regimes. Providing insight into the dynamical processes occurring during processing, and adequately characterizing the kinetic roughening that occurs, present a challenge.

Approach: One way of obtaining this insight is by detailed examination of surface topography data acquired using scanning probe microscopies such as atomic force microscopy (AFM). The complexity of detail inherent in a "rough" surface makes it impossible to characterize roughness observed in the raw surface topography data in terms of the relative importance of dominant dynamical processes, such as diffusion, desorption, etc. However, the molecular-scale phenomena involved in deposition or etching leave a definite signature in the surface morphology. Different processes can, in principal, be distinguished through examination of surface height-correlation functions extracted from raw topography data. For instance, a surface that etches in a purely stochastic manner will exhibit no correlation in height at points separated by distance, r, on the surface, for any $r > 0$. In reality, processes such as diffusion spread information across the surface leading to correlation in the surface height that falls off with distance in a well-defined manner, depending on the process involved in developing the correlation. There has been a burgeoning effort over the past ≈ 5 years, both experimentally and theoretically, to develop models and determine the "scaling" of surface correlation to be expected for various surface dynamical processes and compare these expectations with experiment.

Results and Future Plans: The focus of this work has been on kinetic roughening that occurs during dry etching processes that are vital to semiconductor processing. This is a very complicated environment for which it is difficult to develop *in-situ* probes that could provide the necessary information on surface dynamics. Preliminary studies of GaAs etching in H_2 plasmas have examined changes in surface composition (Auger spectroscopy, photoelectron spectroscopy) and morphology (AFM) as a function of etch conditions - time, temperature, etc. Analysis of the remnant correlations that exist after etching indicate the dominant mechanism influencing surface roughening for long length scales are the desorption processes, leading to logarithmic correlations. However, for distances less than about 30 nm - 50 nm, there is a crossover in the dynamics, most likely to a diffusion dominated regime. Analysis of the temperature dependence of the crossover length may provide information on the relative activation energies for desorption vs. diffusive processes.

In the future, this work will be extended to other etch chemistries while at the same time we will attempt to develop the methodology to extract quantitative kinetic parameters and understand the major sources of bias and uncertainty in the acquisition of experimental data and subsequent analysis.

15. Near-Field Scanning Optical Microscopy Incorporating Raman Scattering for Vibrational Mode Contrast

C.E. Jordan, S.J. Stranick, R.R. Cavanagh, L.J. Richter and D.B. Chase (DuPont)

Objective: To assess near-field scanning optical microscopy incorporating spectral contrast with spatial resolution that is an order of magnitude better than that set by the diffraction limit of light. For many chemical problems, it would be advantageous to use vibrational spectroscopy such as Raman scattering as the optical contrast mechanism.

Problem: In the absence of signal intensification factors, such as 'surface enhancement' or electronic resonance in the specimen, Raman scattering suffers from a small cross section. While there have been reports of Raman-NSOM efforts that exploit specimen-specific intensification, the utility of Raman-NSOM for a wider variety of samples is of great interest.

Approach: Near-field Raman measurements were made using a custom NSOM, configured to allow the collection of reflected and transmitted light. To assess the general applicability of the Raman approach, we have probed diamond films - specimens that should be free of surface and resonance enhancement factors. Raman spectra were recorded as a function of tip-to-sample separation (Z), revealing the Raman active mode at 1332 cm^{-1} corresponding to the diamond crystal phonon. The data points in Fig. 1 indicate the intensity of this phonon mode as the separation distance is increased. The intensity of this mode rapidly decreases and levels off at a separation of ≈ 100 nm. In general, near-fields from an aperture will decay *exponentially* away from the aperture with a characteristic length given by its lateral dimension. We have numerically integrated the field intensity from a near-field aperture over a semi-infinite half-space a distance **Z** from the aperture. For apertures ≤ 40 nm in radius, **a**, the integral decays as exp(-**Z**/**l**) with **l** ≈ **a**/1.5.

Results and Future Plans: The solid lines in Figure 1 are exponential fits to the data with **l** = 34 nm for the transmitted Raman and **l** = 27 nm for the reflected Raman which implies aperture radii of approximately 50 and 40 nm, respectively. By measuring this decay, we are able to approximate the near-field and far-field contributions to the detected Raman intensities. For the Raman Z-scans shown in Fig. 1 the near-field to far-field intensity ratios are 5:1 and 9:1 for transmission and reflection, respectively.

This allows us to assess the near-field and far-field contributions to the measured Raman intensities. The significant near-field contribution indicates that Raman scattering may offer a general approach to vibrationally resolved nanoscale imaging. Our current efforts are directed at the development of robust and reproducible tips that are optimized for their Raman enhancement capabilities.

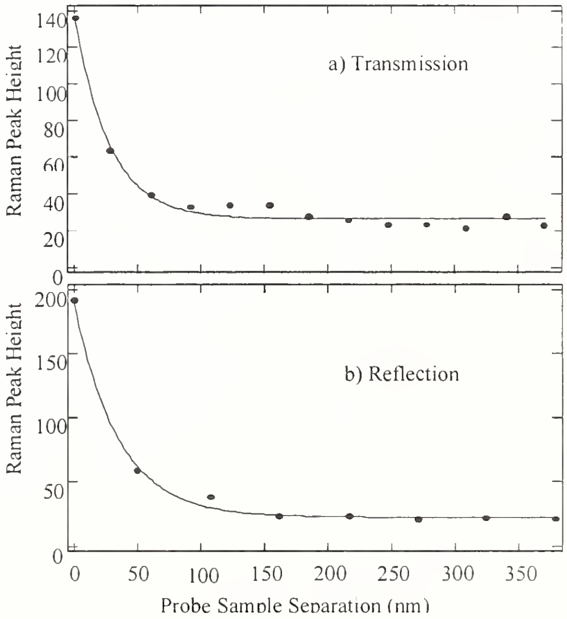


Figure 1. Raman signal for diamond phonon mode as a function of tip-sample separation.

16. Polyatomic Primary Ion Beams for Ultrashallow Depth Profiling of Semiconductors by Secondary Ion Mass Spectrometry

J.G. Gillen

Objective: To develop new ion sources for the generation of novel cluster (and polyatomic) primary ion beams for secondary ion mass spectrometry (SIMS) and to determine the feasibility of using cluster bombardment for semiconductor depth profiling of ultrashallow junctions and implants.

Problem: SIMS is one of the most widely used tools for characterization of dopants in semiconductor materials. As semiconductor device dimensions continue to decrease, improvement in the depth resolution of SIMS depth profiles is needed to characterize ultrashallow dopant implants and junctions as defined by the SIA roadmap. To a first approximation, the resolution of a SIMS depth profile is limited by the depth of penetration of the primary ion beam which, in turn, is directly related to the primary ion energy. The state-of-the-art SIMS method for characterizing ultrashallow implants and junctions is to use low energy (250 eV-500 eV) bombardment with O_2^+ primary ions. Even though impressive results have been obtained in profiling test structures at these reduced bombardment energies, further reduction in primary beam energy may not be practical for routine depth profiling applications due to the increased degradation of the beam quality and focus and a significant reduction in erosion rate of the sample. Furthermore, the majority of existing SIMS instruments are based on magnetic sector mass analyzers that utilize high secondary ion extraction voltages. Operation of these instruments with very low energy primary ion beams is generally not practical for routine analyses.

Approach: A possible solution to this problem is to use cluster or polyatomic primary ion bombardment of the semiconductor sample. When a cluster ion strikes a surface, it dissociates into its constituent atoms. Each of the constituents retains a fraction of the initial energy of the cluster ion given by the simple relationship:

$$E_C = E_o (M_c/M_t)$$

Where E_C is the final energy of an individual constituent atom after collision of the cluster with the surface, E_o is the energy of the cluster ion before impact, M_c is the mass of the constituent and M_t is the total mass of the cluster ion. For example, a C_{60}^- cluster ion with an initial impact energy of 3000 eV would dissociate after impacting the target surface into 60 carbon atoms each with an impact energy of only 50 eV. Because the cluster beam is extracted and focused at keV ion energies, good quality beam focus is maintained, the reduction in erosion rate is not severe and the source can be used in high extraction field SIMS instruments to provide low net bombardment energies.

Results and Future Plans: A modified hot filament duoplasmatron ion source has been constructed for generation of SF_5^+ polyatomic primary ion beams. An evaluation of this novel primary ion beam species for ultrashallow depth profiling has been conducted on a variety of test samples including low energy B implants in silicon, B and Ge delta-doped test structures in silicon and a Ni/Cr depth profiling Standard Reference Material. Most experiments have been conducted using the SF_5^+ ion beam at 3.0 keV impact energy and an incidence angle of 52° with and without oxygen backfill. Preliminary results using the B delta-doped structures indicate that SF_5^+ primary ion bombardment with oxygen backfill gives improvements in trailing edge decay lengths (a measure of the depth resolution of a depth profile) of approximately a factor of 2 compared to O_2^+ bombardment under the same conditions (1/e decay lengths for $SF_5^+ \approx 1$ nm). For depth profiling of metals, the SF_5^+ primary ion beam without oxygen backfill results in a substantial reduction in surface roughness (factor of 6) giving depth profiles comparable to those obtained with O_2^+ bombardment and sample rotation. These studies are being extended by the addition of a second primary ion cluster source that will facilitate evaluation of depth profiling with a wide variety of polyatomic and metal cluster primary ion beams.

17. SF_5^+ *Polyatomic Projectiles for Characterization of Compounds in Model Biological Matrices*

S.V. Roberson and J.G. Gillen

Objective: To improve in sensitivity, stability and specificity of molecular secondary ion mass spectrometry (SIMS) through the use of polyatomic primary projectiles as sputtering sources.

Problem: Static (low dose) SIMS (SSIMS) is the method of choice for desorption of molecular species and is generally used in the analyses of all organic surfaces. Typical SSIMS analysis conditions result in sputtering of only 10 % of the outermost monolayer of a surface. A compound of interest typically has a very dilute distribution (ppm level) in a biological system, a situation that greatly reduces the number of molecules available for imaging. The result is an insufficient number of molecules present in the surface monolayer from which to generate either images or mass spectral information. Thus, sampling into the bulk of the material is necessary for mapping the distribution of a compound in a biological matrix. This molecular depth profiling (dynamic SIMS), however, is synonymous with sputtering beyond the SSIMS limit of 10^{13} ions/cm^2 and leads to rapid decay (fragmentation, damage) of characteristic molecular ion signals.

Approach: The use of polyatomic primary ion sources provides a promising approach for circumventing some of the problems associated with the limited secondary ion signals in SSIMS and the rapid accumulation of damage seen in dynamic SIMS. Utilizing polyatomic ions as primary projectiles in SIMS provides several potential advantages over the use of atomic projectiles. Among these are: increased secondary ion signals, surface localization of damage, sputtering beyond the SSIMS dose limit, and the potential to optimize the primary beam for a given experiment. The Analytical Microscopy Group (in collaboration with Peabody Scientific) has developed a polyatomic primary ion source (generating SF_5^+) for organic SIMS studies on a commercial magnetic sector instrument. The magnetic sector instrument is configured for secondary ion imaging and depth profiling. The SF_5^+ polyatomic projectile was investigated in terms of its usefulness for studying the positive ion emission of neurotransmitters (acetylcholine and glutamate) in model biological matrices (vapor deposited thin films, doped gelatin films, doped rat brain homogenates). Polyatomic ion bombardment of the model matrices was compared with atomic (Ar^+) bombardment under both static and dynamic conditions.

Results and Future Plans: A 10-50 fold enhancement in the secondary ion signal was seen when SF_5^+ was used as the primary projectile in the SSIMS (surface) mode. A depth profile (acquired using dynamic SIMS) of a 220 nm glutamate thin film is shown in Figure 1. The quasi-molecular ion (m/z 148), diagnostic fragments at masses 102 and 84, and the signal from the silicon substrate (m/z 28) were monitored during the course of the experiment. The secondary ion signals obtained by *integrating* over the depth of this film using SF_5^+ were enhanced by as much as a factor of 700 , as compared to Ar^+ bombardment. This work provides the first demonstration of depth profiling through an organic film while maintaining characteristic molecular secondary ion signals. In the future, we plan to utilize a soon-to-be-acquired cesium sputter source for generation of novel negative polyatomic primary ions. This new source is expected to be particularly valuable in the analysis of insulators, such as organics.

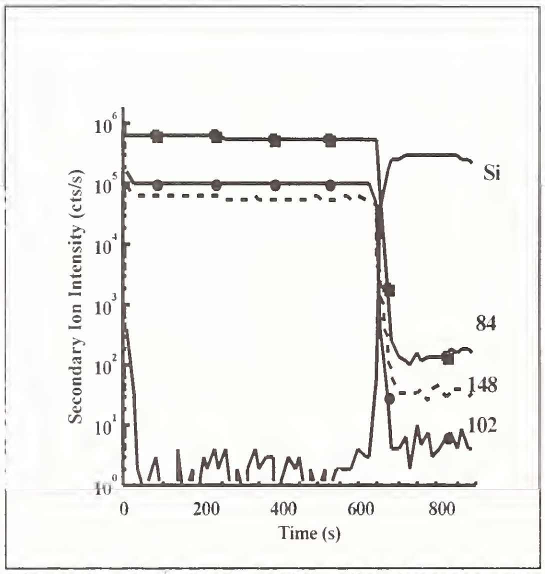


Figure 1. SF_5^+ depth profile of a glutamate thin film.

18. *Certification of SRM 2806, RM 8631, and RM 8632: Contamination Reference Materials for the Fluid Power Industry*

R.A. Fletcher, D.S. Bright, J.A. Small, E.B. Steel, J.R. Verkouteren, E.S. Windsor, W.S. Liggett (ITL)

Objective: To develop and certify a critically important Standard Reference Material (SRM), trace dust particles in hydraulic oil, that serves as the principal reference material for contamination control in the fluid power industry. The SRM is a required test material for both national and international (ISO) standards.

Problem: The National Fluid Power Association asked NIST to develop a SRM to support the fluid power industry. Particulate contamination of lubricants in hydraulic systems is a serious and costly problem that is common to mobile equipment, ships, planes, large vehicles, and machines for manufacturing. Optical particle counters are widely used by the fluid power industry to monitor the particle contamination levels of fluids and to test the capacities and characteristics of filters used in hydraulic systems. We have developed a Standard Reference Material (SRM 2806 Medium Test Dust (MDT) in hydraulic fluid) and two associated Reference Materials (RM 8631 and RM 8632) to be used for calibrating these particle contamination monitoring devices. SRM 2806 will be replacing a test material that has been accepted and used internationally by the industry for over 25 years, and in doing so will advance the measurement accuracy and precision for contamination monitoring applications and liquid particle filter testing. RM 8631 consists of the same mineral dry dust used in SRM 2806. It will allow users to produce transfer standards for calibrating particle counters from a sensor calibrated using SRM 2806. RM 8632 is composed of an ISO ultra fine dry test dust that will be used to verify the performance of optical particle counters.

Approach: Fluid Technology, Inc. (FTI) produced the material in large volumes. A task force composed of members from four corporations and NIST collaborated to solve production problems and to assure a test material of high quality. SRM 2806 was certified at NIST for the total number of particles per milliliter of fluid greater than a specified particle size. The major steps involved in the certification are the following: (1) material homogeneity testing, (2) particle filtration, (3) electron microscopy to obtain digital images of the separated material, (4) image analysis to provide the size distribution and (5) data/uncertainty analysis. Homogeneity testing was conducted using a calibrated optical particle counter to determine the sample-to-sample uniformity on a relative basis. Particles were quantitatively filtered from selected samples for microanalysis. Scanning electron microscopy and image processing were used to certify this material. Analysis was performed using statistical methods that included kriging and cubic spline fitting. Uncertainties in the measurements resulting from the microscopy, image processing, digitization and fluid volume extraction were taken into account.

Results and Future Plans: Certification of SRM 2806 and testing of the two RM's were completed this year and the materials are now available for use by the fluid power industry. SRM 2806 and RMs 8631 and 8632 are required materials in the national standard method NFPA/T2.9.1 R2 and the international method ISO/FDIS 11171, and they impact numerous ISO documents related to fluid power. U.S. industry and NIST collaborated to take the lead in establishing contamination control standards for the world. Future efforts will be directed to extend the range of the certified size distribution and possibly to develop another SRM material to satisfy special requirements for the aeronautical industry.

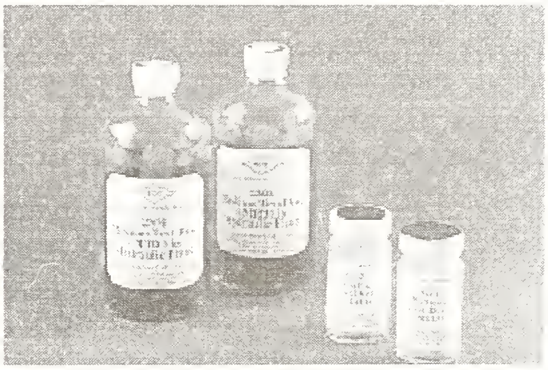


Figure 1. SRM 2806 particle-in-oil , RM 8631 and RM 8632.

19. Low Background Substrates for Microanalysis

E.S.Windsor, S.A. Wight, C.J. Zeissler, E.B. Steel and D.H. Blackburn

Objective: To prepare substrates for microanalysis that can be used for multiple analysis techniques.

Problem: Microanalysis often involves the use of several different techniques to analyze a particle sample. Analysis frequently begins with the light microscope and then proceeds to X-Ray, electron and ion beam instruments. Sample substrates usually differ for these techniques. Samples prepared for light microscopy are mounted on glass microscope slides that allow transmitted light analysis and phase identification. However, the glass microscope slide is not a suitable substrate for electron or ion beam techniques in which elemental chemical information is obtained because glass slides typically contain elements (Si, Na, K, Mg, Al and O) that interfere with the analysis of an unknown. To eliminate these interferences, samples for electron and ion beam techniques are typically mounted on carbon planchets. In this protocol, samples that are first prepared for light microscopy must be transferred to other substrates before applying the elemental techniques. This is a time consuming and difficult process during which particles of interest may be lost.

Approach: Specialty glasses have been prepared at NIST that allow samples to be analyzed using multiple microanalysis techniques without the need for sample transfer and remounting. These substrates are borate derivative glasses made to contain only low atomic number elements that minimize interference when used in electron and ion beam instruments. Borate glass is not stable under atmospheric conditions and therefore additional material must be added for stability. Historically, lithium and beryllium were added but concerns over beryllium toxicity have persuaded us to search for other stabilizing additives.

Results and Future Plans: We have synthesized a lithium borate glass stabilized with MgO and SiO_2. In Figure 1, the X-Ray spectrum obtained from this substrate is compared with those of a typical silica glass slide and a beryllium-stabilized lithium borate glass. The beryllium-stabilized glass is the ideal substrate for this application since it contains no X-Ray peaks over the entire energy range. The X-Ray peaks observed in the spectrum of the silicate glass slide could interfere with the analysis of an unknown placed upon this substrate. The Mg- and Si-stabilized glass offers a large improvement over the silica glass slide, although it still contains two small peaks (Mg and Si) in the low energy range of the spectrum. In the future we plan to try to eliminate the silica from the Mg-Si- stabilized glass thereby reducing the interference to that of a single known concentration of Mg. We will also experiment with other compositions to determine whether they stabilize the glass. Scandium oxide, for example, would be a good choice since scandium is rarely present in the samples that we encounter. Some of these glass compositions may be of commercial interest to laboratories performing microanalysis.

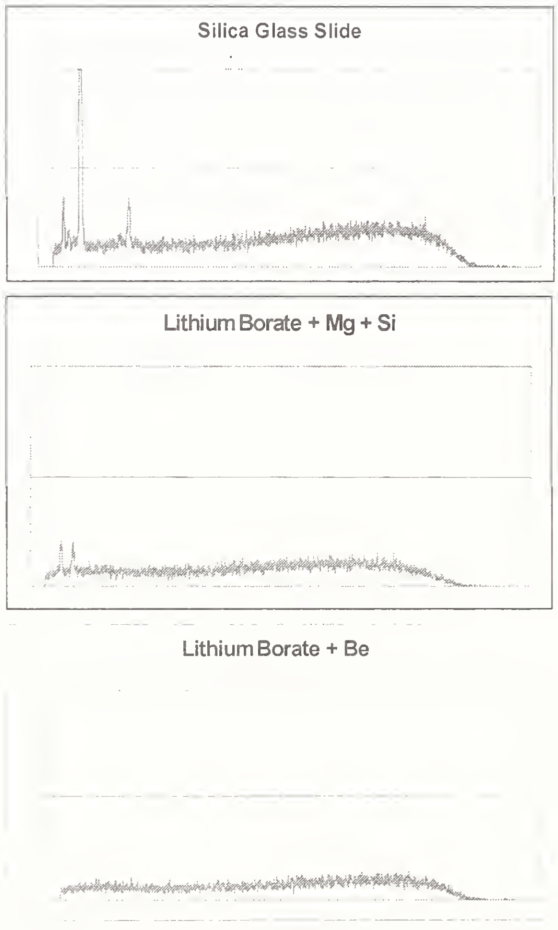


Figure 1. Energy dispersive X-Ray spectra for 3 different glass substrates. Plots are the same scale and show X-Ray counts plotted on the y axis vs.increasing X-Ray energy plotted on the x axis.

20. SRM 1922: A Mineral Oil Refractive Index Standard for the Calibration of Refractometers

J.R. Verkouteren and E.B. Steel

Objective: To provide a standard for the calibration of refractometers targeted at the measurement of the sugar content of solutions.

Problem: The determination of the sugar content of solutions is routinely accomplished through the measurement of refractive index. The weight percent of sugar in water is determined from the refractive index using the well established convention of the Brix scale. The concentration of sugar in solution is of interest to the manufacturers of corn syrup, whose goods are priced according to sugar concentration. Since the goods are sold in very large quantities, small differences in sugar concentration translate into large differences in price. Sugar solutions are not appropriate as refractive index standards due to their long-term instability. A standard was required for the calibration of refractometers that would fall within the range of measurements applicable to the Brix scale, and would have the necessary attributes of a standard, such as homogeneity and stability. In addition, it was important to choose a liquid as a standard, rather than a glass (which is more typical for a refractive index standard), due to the prevalence of refractometers designed exclusively for liquids and for comparability with sugar solutions. Liquids are more challenging as refractive index standards due to a large coefficient of change with respect to temperature. The dependence of refractive index on temperature for normal ambient ranges (15 °-35 °C) must be characterized and provided as a certified value.

Approach: A mineral oil was selected for the standard because of a number of desirable traits: 1) the refractive index falls within the range of sugar solutions, 2) the oil is non-volatile and is expected to be stable with respect to composition, and 3) the material was readily available in large quantities. The mineral oil was poured into 500, 30 cc amber glass bottles with teflon-lined screw-top lids, and a random set was selected for characterization. The measurements of refractive index were conducted on a precision goniometer using the classical method of minimum deviation. A Cd lamp was used for measurements at 643.8 nm, 508.6 nm, 480.0 nm, and 467.8 nm, and a Hg lamp was used for measurements at 546.1 nm. The refractive index at 589.3 nm was determined by a fit of a standard dispersion equation to the measured data. The measurements were performed at 5 temperatures between 15 °C and 35 °C. The mineral oil was contained in a glass prism and the temperature was controlled by a water bath. The temperature of the oil was measured with a precision of ±0.1 °C. Initial measurements indicated the presence of a temperature gradient within the volume of liquid. To alleviate the problem, a system was devised to stir the liquid during the measurements of refractive index. The homogeneity of the oil was tested by measurements on multiple aliquots, using both the minimum deviation technique and an Abbe-type refractometer. Statistical analysis was performed to determine uncertainties for the certified values, which were calculated as centered 95 % (2-σ) prediction intervals.

Results and Future Plans: SRM 1922 is ready for delivery. The certified values include the refractive indices at a range of wavelengths, and the change in refractive index with temperature. The certified value of refractive index at 589.3 nm is $1.4676 \pm 1.0 \times 10^{-4}$, which is equivalent to a Brix value of 74 %, and the change in refractive index with temperature is $-3.7 \times 10^{-4} \pm 1.0 \times 10^{-5}$/°C. The most typical refractometers are readable to one part in 10^{-3}, and therefore the uncertainties in the certified values are well within the needs of the measurement community. The refractive index can be calculated for temperatures between 15 °C and 35 °C, which allows the calibration to be performed under a range of normal ambient conditions. This standard should supply the community for many years to come.

21. *Isotope Ratio Measurements by Time-of-Flight Secondary Ion Mass Spectrometry*

A.J. Fahey and S. Messenger

Objective: To develop experimental protocols and data processing procedures so that precise and accurate isotopic ratios can be obtained from submicrometer regions of solids by time-of-flight secondary ion mass spectrometry (ToF-SIMS).

Problem: Modern ToF-SIMS instruments use finely focused Ga^+ ion beams with diameters of ≈100 nm and primary ion pulse lengths of < 1 ns to remove very little material from the sample under analysis. ToF-SIMS has not been considered capable of producing accurate and precise isotope ratio measurements because of the low duty cycle of the primary ion beam ($\approx 10^{-5}$) and the resultant low secondary ion count rate. However, for certain problems involving the measurement of isotope ratios where very little material is available and measurement uncertainties of ≈1 % are sufficient, ToF-SIMS is a viable technique. One such problem is the measurement of refractory meteoritic material that condensed in regions around distant stars before the solar system formed. This material typically consists of mineral grains that are ≈1 µm in size and have isotopic ratios that differ from terrestrial values by up to 1000 %.

Approach: To develop the technique and software needed to measure isotope ratios on very small spatial scales with the ToF-SIMS, Si isotopes were measured on commercially produced SiC powder that has a 1–2 µm grain size. Temporally interlaced sputtering was used to reduce the production of secondary hydride ions. An O_2^+ sputter beam was rastered over a 200 x 200 µm area to clean the surface while a finely focused Ga^+ ion beam was used for analysis. Software was developed to read in the spectral data files produced by the instrument in order to make corrections and to form the ratios properly. The process is iterative and involves correction for dead time, stripping of the $^{28}SiH^+$ peak from the $^{29}Si^+$ signal, and proper integration of the peaks. Once the software was written, the correct dead time was determined by analyzing data for a range of dead-time values and determining at which dead time the measured ratios intersected the terrestrial mass fractionation line. The data for the Si isotope dead-time determination are shown in Figure 1 plotted as part-per-thousand (per-mil) deviations from the terrestrial ratios. One can see that the fitted line intersects the mass fractionation line at ≈70 ns.

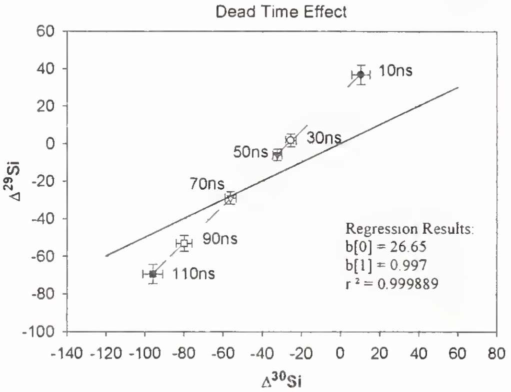


Figure 1. Dead-time effect for Si isotopes measured by ToF-SIMS.

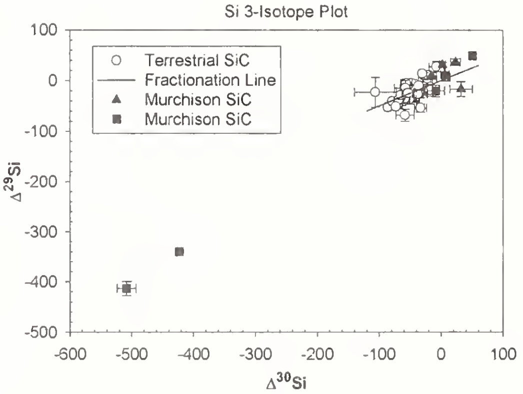


Figure 2. Si isotopes in terrestrial and meteoritic SiC measured by ToF-SIMS.

Results and Future Plans: The ToF-SIMS methodology was applied to the measurement of SiC particles separated from the Murchison meteorite. A great deal of data from Murchison SiC has been taken on magnetic sector instruments that can be used for comparison. The data obtained by ToF-SIMS at NIST are shown in Figure 2. Terrestrial SiC particles were measured and plot near the origin along a mass fractionation line of slope ½, as expected. SiC grains measured from Murchison are also plotted. Most data points lie above and to the right of the terrestrial data, however two unusual grains are highly depleted in ^{29}Si and ^{30}Si. These depletions have been observed previously by others and it is thought that these grains originated in the atmospheres of supernovae.

V. Physical and Chemical Properties Division (838)

Richard F. Kayser, Chief

A. Division Overview

Mission

The Physical and Chemical Properties Division is the Nation's reference laboratory for measurements, standards, data, and models for:

- the thermophysical and thermochemical properties of gases, liquids, and solids – both pure materials and mixtures,
- the rates and mechanisms of chemical reactions in the gas and liquid phases, and
- fluid-based physical processes and systems, including separations, low-temperature refrigeration, and low-temperature heat transfer and flow.

The Division provides technical research and services, Standard Reference Data, Standard Reference Materials, and calibrations to promote U.S. economic growth and to assist U.S. industry, other government agencies, and academia in solving problems of national importance.

Functions

In the areas of thermophysics, thermochemistry, and kinetics, the Division:

- develops, maintains, and uses state-of-the-art apparatus to perform experimental measurements on industrially and scientifically important systems,
- compiles, evaluates, and correlates experimental data,
- develops and evaluates state-of-the-art theories, models, estimation methods, and computational approaches, and
- disseminates results by a wide variety of mechanisms.

In the area of cryogenic technologies, the Division provides engineering data, models, and research to support the development of advanced cryocoolers, and measurement methods, standards, and services for flow under cryogenic conditions.

Current Focus Areas

Current focus areas include *Basic Reference Data and Computational Techniques*, *Data for Process and Product Design*, *Properties of Energy-Related Fluids*, *Environmental Fates of Industrial Chemicals*, *Tools for Chemical Analysis*, *Fundamental Studies of Fluids*, and *Cryogenic Technologies*. Brief descriptions of these areas follow, with references to selected Technical Highlights (see next section).

Basic Reference Data and Computational Techniques

Physical, chemical, and kinetic data and models are important in research and development, process modeling, process design, energy efficiency, safety, health, transportation and storage, custody transfer, and the environment. Scientists and engineers require sufficient data for many substances to determine parameters in commonly used models, to develop new and improved estimation methods and models, and to evaluate and compare estimation methods, models, and computational techniques. The principal components of this program are:

- to compile, evaluate, and disseminate data and predictive methods for chemical species and systems of broad interest to a large number of diverse users and
- to develop, apply, and assess computational approaches for acquiring such data.

During 1997, the Division initiated a new program in quantum chemistry focused on the development of resources to aid industrial scientists and engineers in the computation of molecular properties. These resources will include (a) critical comparisons of computational results with the best available experimental data, (b) interactive guidance for the non-expert on methods, reliability, and resource requirements, and (c) a searchable repository where scientists may submit or extract the results of standard calculations. During 1998, the Division developed plans to develop the next-generation chemical kinetics database. This effort will involve significant emphasis on the critical evaluation of data, the use of results from computational chemistry, and the development and validation of theoretically-based data prediction methods. For additional information on *Basic Reference Data and Computational Techniques*, see Technical Highlights 1-8 and 32.

Data for Process and Product Design

Process and product design in a wide variety of industries depends on the availability of high-quality physical and chemical properties data and models. The availability of such information has played a key role in the emergence of process simulators as a key enabling technology in the chemical and related industries. Large-scale process modeling and simulation is also growing in importance in areas such as semiconductor processing and the treatment of hazardous wastes. The Division's goal is to provide the underlying data and models needed to support such developments. Areas of current interest include:

- semiconductor processing
- chemical and materials processing
- separations, including distillation, extraction, adsorption, and membrane separations
- advanced oxidation technologies
- combustion.

For additional information, see Technical Highlights 9-13.

Properties of Energy-Related Fluids

Industry requires accurate and comprehensive equilibrium and transport properties data and models for energy-related fluids in several key areas, including the design and optimization of working cycles in refrigeration systems and power plants; the design, control, and optimization of gas processes; and custody transfer. Efforts in this area include the development of experimental apparatus, the acquisition of needed data, and the development and dissemination of high-accuracy correlations. Fluids under study include

- natural gas systems,
- alternatives to ozone-depleting chlorofluorocarbons and hydrochlorofluorocarbons for use in air-conditioning and refrigeration systems,
- alternatives to steam for use in power cycles, e.g., ammonia-water mixtures, and
- noble gas mixtures for use in thermoacoustic refrigerators.

During 1998, the Division expanded its experimental and modeling research on the properties of natural gas systems. Major goals of the program are to develop the means to accurately model and predict the thermodynamic, phase equilibrium, and transport properties of natural gas, liquefied natural gas (LNG), natural gas liquids (NGLs), substitute/synthetic natural gas (SNG), compressed natural gas (CNG), and wet, dry, and sour gases. For additional information on *Properties of Energy-Related Fluids*, see Technical Highlights 14-18.

Environmental Fates of Industrial Chemicals

A wide variety of physical, chemical, interfacial, and kinetic data and data prediction methods are essential to understand and assess the long-term fates of new and existing chemicals in the atmosphere and in ground water. Properties of interest include atmospheric lifetimes, aqueous solubilities, ion-exchange equilibria, and partition coefficients. Current efforts are focusing on:

- the atmospheric chemistry and lifetimes of alternative refrigerants, alternative fire suppressants, and oxygenated fuel additives and
- the thermodynamics and kinetics of selected species in aqueous solution.

During 1997, the Division initiated a multi-year program on thermodynamic properties for environmental fate and risk analysis, with the principal emphasis on heavy-metal-containing species and the common ions with which these species come into contact in aqueous environments. This program will comprise: (a) an assessment and analysis of the state of the literature regarding selected species and properties, (b) the development of needed experimental capabilities, (c) the acquisition of experimental data to fill gaps and resolve discrepancies in the data, (d) the development of comprehensive models for the thermodynamic properties of "key substances", and (e) the construction of a data-handling system to manage the resulting network of thermodynamic information in a thermodynamically consistent manner. For additional information on *Environmental Fates of Industrial Chemicals*, see Technical Highlights 19-20.

Tools for Chemical Analysis

The analysis of simple and complex mixtures and the identification of individual chemicals are tasks central to many aspects of the chemical and related industries, including research and development, production, and quality assurance and control. These tasks are also crucial in environmental monitoring, medical research, and health care. In this area, the Division strives to produce critically evaluated data, predictive models, and software to assist in the analysis and identification of as wide a range of species as possible. Areas of current emphasis include:

- mass spectral (MS) data and databases,

- gas chromatographic (GC) data and databases,
- infrared data and databases,
- tools for automatically deconvoluting, and analyzing GC/MS data files.

In the latter area, the Division is working with the U.S. Defense Threat Reduction Agency, the Organization for the Prevention of Chemical Weapons, and others to develop software for use in on-site inspections under the Chemical Weapons Convention. For additional information, see Technical Highlights 21-22.

Fundamental Studies of Fluids

The goals of this program are to develop and use unique experimental, theoretical, and simulational capabilities to study fluid systems under equilibrium and non-equilibrium conditions, with and without chemical reactions. Topics under investigation include:

- development of evanescent-wave cavity-ring-down spectroscopy for studying chemical reactions at interfaces,
- the effects of shear on the microscopic structure of colloids, gels, micelles, and emulsions and on the dynamics of processes such as coagulation, gelation, and association,
- molecular dynamics studies of chromatographic retention mechanisms,
- fluid-solid phase transitions, and
- new approaches to primary standards for temperature and pressure.

For additional information, see Technical Highlights 23-29.

Cryogenic Technologies

Cryogenic technologies such as pulse-tube refrigerators underpin a wide variety of technically important areas. These areas include the cooling of electronics for high-speed computing and communications, the production of ultra-clean environments for semiconductor processing, the liquefaction of natural gas from remote gas wells and for use as a clean fuel, the cooling of medical instruments, and the cooling of satellite-based infrared sensors for military and environmental applications. Research in this program addresses all of these topics, with the primary focus on:

- the development of improved measurement and modeling techniques for characterizing basic cryocooler components and processes in the temperature range from 120 K to below 10 K,
- collaborations with industry and others to support the development of cryocoolers for specific applications, and
- the measurement of cryogenic flows.

During 1997, the Division initiated a new program in microscale heat transfer. The goal is to develop and validate models and correlations for predicting heat transfer between fluids and solids when the length or time scale over which the heat transfer takes place becomes very small. For additional information, see Technical Highlights 30-31.

Selected Technical Highlights

- Major upgrade of NIST Standard Reference Database (SRD) 4: Thermophysical Properties of Hydrocarbons and release of first version of SRD 72: NIST Thermophysical Properties of Air and Air Component Mixtures (AIRPROPS) (see Technical Highlight 2)
- Definitive measurements of the dielectric constant of liquid water at its saturated vapor pressure between 1 °C and 145 °C (4)
- Major upgrade of NIST SRD 17: Chemical Kinetics and development of new tools for analyzing complex unimolecular and recombination reactions (6)
- Measurement of the Kamlet-Taft solvatochromic parameters for an extensive set of glycol ethers and glycol ether aqueous solutions (10)
- Lead authorship of chapter on “Short-Lived Ozone-Related Compounds” in 1998 International Scientific Assessment of Ozone Depletion (19)
- Major upgrade of SRD 23: NIST Thermodynamic and Transport Properties of Refrigerants and Refrigerant Mixtures (REFPROP) (16)
- Major upgrade of SRD 1: NIST/EPA/NIH NIST Mass Spectral Database – NIST 98 (21)
- Release of Automated Mass Spectral Deconvolution and Identification System for automatically deconvoluting and analyzing complex GC/MS data files (22)
- Experimental and theoretical elucidation of the effects of shear on the microscopic structure and dynamics of gelling systems (24)
- Acquisition of comprehensive data on the thermal conductances of packed lead spheres needed for the optimal design of regenerative heat exchangers used in cryocoolers and cryopumps (30).

Selected Conferences and Workshops

Major international conferences:

- NATO Advanced Study Institute on *Energetics of Stable Molecules and Reactive Intermediates*, July 9-24, 1998, Castelo Branco, Portugal (Technical Highlight 32)

Topical meetings:

- DIPPR Liaison Forum, November 17, 1997, Los Angeles, CA
- Meeting of International Energy Agency Annex 18 on the Thermophysical Properties of the Alternative Refrigerants, June 8, 1998, Trondheim, Norway

Workshops:

- Workshop on Chemical Databases for Combustion Modeling and Simulation, September 28, 1998, Gaithersburg, MD.

Organizational Structure

The Physical and Chemical Properties Division has research groups in Gaithersburg, Maryland and Boulder, Colorado, with the equivalent of 35-40 full-time employees in each location. Dr. William M. Haynes directs the Boulder part of the Division. The structure and technical activities of the Division are as follows:

Division-Office Programs (Gaithersburg and Boulder)

- Study the behavior of fluid systems under both equilibrium and non-equilibrium conditions using unique experimental, theoretical, and simulational capabilities.

Process Separations Group (Boulder)

- Performs basic and applied research on a variety of separation processes, including distillation, supercritical fluid extraction, adsorption, and membrane separations
- Provides critically-evaluated data and models needed to design and/or select more efficient and robust separation processes.

Fluid Science Group (Gaithersburg)

- Develops and applies state-of-the-art techniques based on acoustics and other novel approaches for measuring the thermodynamic and transport properties of fluids and fluid mixtures, including refrigerants and semiconductor processing gases
- Performs research on next-generation primary standards in the areas of temperature, pressure, and low flow rate.

Experimental Kinetics and Thermodynamics Group (Gaithersburg)

- Develops and uses state-of-the-art measurement techniques to determine the rates and mechanisms of chemical reactions in the gas and liquid phases and the thermodynamic properties of industrially and environmentally important chemical species and materials
- Develops new measurement methods for detecting and characterizing reactive intermediates
- Certifies Standard Reference Materials for thermodynamic properties important to industry and science.

Chemical Reference Data and Modeling Group (Gaithersburg)

- Develops and evaluates new theories, models, and estimation methods for thermodynamic properties, rate constants, and molecular spectra
- Compiles, evaluates, correlates, and disseminates Standard Reference Data
- Develops and disseminates electronic databases and software on thermodynamics, chemical kinetics, and analytical mass and infrared spectra.

Computational Chemistry Group (Gaithersburg)

- Develops and applies computational methods for calculating the chemical and physical properties of selected species and systems
- Critically compares computational predictions with the best available experimental data to establish the accuracy and reliability of computational methods
- Develops resources to provide guidance to non-experts on methods, reliability, and resource requirements.

Experimental Properties of Fluids Group (Boulder)

- Performs experimental research and develops and maintains high-accuracy apparatus for measuring the full complement of thermodynamic and transport properties of fluids and fluid mixtures over wide ranges of temperature, pressure, and composition
- Provides comprehensive thermophysical property measurements for technically important pure fluids and mixtures, including common organics and inorganics, hydrocarbons, refrigerants, and aqueous systems.

Theory and Modeling of Fluids Group (Boulder)

- Performs theoretical and simulational research on the thermophysical properties of fluids and fluid mixtures, including regions of fluid-fluid and fluid-solid phase separation
- Develops models and correlations of high accuracy to describe and predict the thermophysical properties of fluids and fluid mixtures
- Provides comprehensive and evaluated Standard Reference Data and electronic databases for the properties of technically important fluids and fluid mixtures.

Cryogenic Technologies Group (Boulder)

- Develops improved measurement and modeling techniques for characterizing basic cryocooler components and processes
- Develops state-of-the-art cryocoolers for specific applications
- Provides measurement standards and services for flow under cryogenic conditions.

Staff Recognition for Fiscal Year 1998

- W. Gary Mallard, Department of Commerce Silver Medal for developing the NIST Chemistry WebBook, the world's most comprehensive collection of chemical reference data available on the Internet
- Robert F. Berg, Department of Commerce Bronze Medal for measuring the viscosity of xenon near its critical point with unprecedented accuracy onboard the Space Shuttle
- Robert E. Huie and Wing Tsang, Research and Development Achievement Award of the Army Research Laboratory for work on halon replacements for ground fighting vehicles
- Karl K. Irikura, NIST Chapter of Sigma Xi Outstanding Young Scientist Award for research on computational thermochemistry
- Peter J. Linstrom, NIST Measurement Services Award for designing the structure of the NIST Chemistry WebBook
- Andrew C. Pipino, Jeffrey W. Hudgens, and Robert E. Huie, CSTL Technical Achievement Award for developing evanescent-wave cavity-ring-down spectroscopy as a new tool for studying chemical reactions at interfaces
- Stephen E. Stein and W. Gary Mallard. NIST Slichter Award for building close ties between the manufacturers and users of mass spectrometers and NIST.

B. Selected Technical Reports

1. The NIST WebBook - NIST Chemical Reference Data for Industry

W.G. Mallard, P.J. Linstrom, J.F. Liebman (UMBC), H. Affefy (UMBC), and P.J. Christian

Objective: To provide Internet access to a complete set of chemical data with a common interface that provides both ease of use and a simple method to expand as more data become available.

Problem: There is an enormous amount of organic thermochemical data (heats of formation, entropies, heat capacities, heats of reaction) that are largely unknown to the technical community. One part of this project is to find and evaluate those data. In addition, there is a need to make available ancillary thermochemical data such as phase-change enthalpies. Data on infrared (IR), ultraviolet (UV) and mass spectra, and other analytical techniques are also important resources that are often difficult to find. For all of these data, it is essential that tools be provided to make the data easy to access.

Approach: The rapid growth of the World Wide Web has been widely remarked upon. Although the most enthusiastic appraisal of the future of the Web may be unrealistic, it is clear that the Web has dramatically changed the way that science is communicated. What has not followed is the development of data resources for the Web, and the WebBook is an effort to correct this. The WebBook provides a quick and direct source of data available at all times. The initial efforts have been tied to an approach based on compounds rather than properties. All the data on benzene, for example, are gathered together, rather than all the data on heat of combustion. While the major thrust of the WebBook is to supply data from NIST evaluations, the role of the WebBook in providing a resource for chemical data from all sources will expand. In parallel with the efforts to gather and evaluate data, another major part of this project is aimed at providing the mechanisms needed to make these and other NIST chemical reference data available on the Internet. These efforts are part of NIST's program on Systems Integration for Manufacturing Applications (SIMA).

Results and Future Plans: During 1998 the fourth edition of the NIST Chemistry WebBook* was released. The total number of compounds for which data is provided has steadily increased and in the fourth edition data for more than 31,600 compounds are available. As with every release to date, additional data types were added – vibrational and electronic data on ions and radicals and spectroscopic constants for diatomic molecules. The fifth release will incorporate corrected and updated vapor pressure data, Henry's law data, critical constant data, as well as significant increases in data for many of the thermodynamic data types already present. A new tool for substructure searching using chemical structures drawn by the user is also being added. The WebBook has been extremely well received: usage has grown greatly both in number of users and number of repeat users. The number of users and the variety of users - both in industry, government and academia - is a clear indication of the need for this type of service; between 5000 and 8000 users per week use the Chemistry WebBook, and the fraction of returning users is 45 % to 55 %. The WebBook is also a tool to aid future evaluation projects both at NIST and in collaborations with others. The goal of this project is to have a single point of entry for access to all chemical data at NIST.

*http://WebBook.nist.gov

Publications:

Linstrom, P.J. and Mallard, W.G., ***"The NIST WebBook: A Tool for Chemical Data Access on the Internet,"*** Proceedings of the 10th International Chemical Information Conference and Exhibition, Nimes, France, October 18-21, 1998.

Mallard, W.G., Linstrom, P.J., Afeefy, H.Y., Liebman, J.F., Stein, S.E., Domalski, E.S., Hearing, E.D., Lias, S.G., Rosenstock, H.M., Draxl, K., Steiner, B.W., Herron, J.T., Holmes, J.L., Levin, R.D., Kafafi, S.A., Hunter, E.P., Chickos, J.S., and Brown, R.L., ***"The NIST Chemistry WebBook,"*** NIST WWW Site - http://WebBook.nist.gov.

2. *Database Activities of the Fluid Properties Data Center*

***D.G. Friend**, M.L. Huber, E.W. Lemmon, A.H. Harvey, J.C. Rainwater, G.R. Hardin, and M.O. McLinden*

Objective: To provide science and industry with the fluid property information needed for commerce, innovation, and efficiency in a broad variety of applications.

Problem: Pure fluids and fluid mixtures are found in many industrial processes as working fluids, solvents, commodity products, fuels, etc. In order to optimize processes which use these fluid systems, to achieve equity in the commercial transfer of important fluids, and to reach consensus in the design and commercialization of systems, it is necessary to have a standard reliable source for the thermophysical properties of the fluid components.

Approach: The Data Center maintains strong contacts with industrial users in such industries as aerospace, cryogenics, petroleum and petrochemical, power, and refrigeration to assess and prioritize their current and anticipated fluid property requirements. As important classes of fluids are identified and ranges and uncertainty parameters are established, projects can be developed to collect and evaluate the data available in the literature, to coordinate necessary experimental measurements within the Division or elsewhere, and to develop the required models and correlations based on the most appropriate theoretical approaches. The dissemination of the results is typically through computer databases and other publications and tabular material.

Results and Future Plans: The major outputs of these efforts are the computer databases distributed by the Standard Reference Data Program of NIST. The Data Center currently supports six distinct computer packages and also contributes to the NIST Chemistry WebBook. Several of these products are connected with other technical highlights included in this Report, and are discussed in the relevant sections. During 1998, the Data Center has been responsible for upgrades of the NIST Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Database (SRD 23, Version 6.01), the NIST/ASME Thermophysical Properties of Water Database (SRD 10, Version 2.1), and the NIST Thermophysical Properties of Hydrocarbon Mixtures Database (SRD 4, Version 2.0), as well as development of the new NIST Thermophysical Properties of Air and Air Component Mixtures Database (SRD 72, Version 1.0).

The SRD 4 program, also known as NIST SUPERTRAPP, allows predictive calculations of the thermodynamic and transport properties of pure and mixed hydrocarbon systems; it now has a component library of nearly 200 species, and the user can add fluids to the database with a minimum amount of information required to achieve reasonable property predictions. The database is based on an extended corresponding states algorithm developed, in part, at NIST.

The program for air (SRD 72, or NIST AIRPROPS) is based, in part, on work done several years ago in conjunction with the National Aerospace Plane project, which included extensive experimental measurements at NIST. The basic air equation is an optimized representation of the experimentally determined thermodynamic surface, and other mixture properties as well as the transport properties are based on an extended corresponding states model related to the model used in SRD 4.

We are currently working on improvements in the mixture models, in conjunction with our projects on natural gas systems and refrigerants, in addition to updated standards for the key pure fluid surfaces and a new database for ammonia-water mixtures. A new graphical user interface has been developed which can incorporate all of the required features associated with all of the Data Center Standard Reference Data programs.

3. *Property Standards for Water and Steam*

A.H. ***Harvey,*** *D.G. Friend, A.P. Peskin, M.A. Killeen, J.M.H. Levelt Sengers, J.S. Gallagher, and S. Kiselev (Inst. Oil & Gas Res., Russia)*

Objective: To provide industry and researchers with standardized properties of water and aqueous mixtures by playing a leading role in national and international property standardization efforts.

Problem: Water, either as a liquid or in the form of steam, plays a vital role in many industrial processes and at least some role in most others. In order to optimize these processes, it is important to have accurate thermophysical properties. In addition, it is desirable for companies to have a standardized set of properties so their designs can compete fairly for contracting, etc. These needs are particularly critical in the steam power industry, where small differences in steam properties may translate into millions of dollars worth of plant performance. Also, since water is widely used in scientific research (both directly and as a calibration fluid), there is a need to supply researchers with the most accurate properties, including quantities such as the dielectric constant and refractive index.

Approach: NIST's efforts are coordinated with the International Association for the Properties of Water and Steam (IAPWS) and with the U.S. National Committee to IAPWS, which is an ASME Research and Technology subcommittee. We provide expertise to these organizations, assist in the dissemination of standards both worldwide and to U.S. industry, and carry out selected research projects to advance the state of understanding of the properties of water and aqueous mixtures.

Results and Future Plans: A revised formulation for the refractive index of water has brought the formulation up to date with the current standard for thermodynamic properties, greatly improved the results in low-temperature and supercooled water, and resolved some issues about the refractive index in the near infrared. We are also participating in an international effort to produce new standard formulations, reflecting both better data and better theoretical understanding, for the thermal conductivity and viscosity of water. Recently, IAPWS has adopted both a new formulation for the thermodynamic properties of water for general and scientific use and also a specialized "industrial" formulation for the needs of the steam power industry. In support of the general and scientific formulation, NIST has developed a user-friendly program for the calculation of a wide variety of properties from this formulation (and from the IAPWS standards for other properties). We have also produced printed Steam Tables as a NIST Internal Report. For the "industrial" formulation, we have tested the computer program distributed by ASME and are participating in the preparation of articles to educate industrial users about the factors they must consider in switching to the new standard. A NIST author will be a Senior Editor for the new edition of the ASME Steam Tables book, which is widely used by mechanical engineers. In the area of aqueous mixtures, theoretical and modeling work is underway or planned on the properties of ammonia-water mixtures, gaseous air-water mixtures, mixtures of ordinary and heavy water, and the solubility of gases in water.

Publications:

Harvey, A.H., Peskin, A.P., and Klein, S.A., ***"NIST Standard Reference Database 10: NIST/ASME Steam Properties, Version 2.1,"*** National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg, MD (1997).

Harvey, A.H., Gallagher, J.S., and Sengers, J.M.H. Levelt, ***"Revised Formulation for the Refractive Index of Water and Steam as a Function of Wavelength, Temperature, and Density,"*** J. Phys. Chem. Ref. Data 27, 761 (1998).

Kiselev, S.B and Friend, D.G., ***"Revision of a Multiparameter Equation of State to Improve the Representation in the Critical Region: Application to Water,"*** Fluid Phase Equil. (in press).

4. *Dielectric Constant of Water*

M.R. Moldover, J. Hamelin (Guest Researcher), and J.B. Mehl (University of Delaware)

Objective: To measure $\varepsilon(T)$, the dielectric constant (relative electric permittivity) of water at its saturated vapor pressure as a function of temperature.

Problem: The derivative $(\partial^2\varepsilon/\partial T^2)_P$ plays an important role in solution thermodynamics. Thus, $\varepsilon(T)$ of liquid water below its boiling point has been measured at least 12 times during the past 50 years. Nevertheless, substantial discrepancies exist between data sets that reviewers have been unable to resolve. The phenomena of electrode polarization and ionic relaxation complicate the interpretation of $\varepsilon(T)$ data taken at low frequencies. At very high frequencies, dielectric relaxation complicates the interpretation of $\varepsilon(T)$ data.

Approach: We developed a novel, two mode, radio-frequency, reentrant resonator to measure the dielectric constant of water at two frequencies: $216/\sqrt{\varepsilon}$ MHz and $566/\sqrt{\varepsilon}$ MHz. These frequencies are high enough that electrode polarization and ionic relaxation are negligible and low enough that dielectric relaxation is also negligible. In contrast with previous apparatus in this frequency regime, the NIST resonator had a thick gold plating on its interior surfaces. With the plating, the microwave skin depth (and the depth-dependent frequency shifts and quality factors Q of the resonances) varied in a predictable way with frequency and temperature. A predictable skin depth was essential for obtaining accurate values of $\varepsilon(T)$ at radio frequencies. The thickness of the skin depth was verified by measuring the Q of each mode. A model equivalent circuit for the resonator that accounted for the loading of the resonator by the external instrumentation was developed. We verified that the model circuit accounted for the conductivity of the water by deliberately adding salt to "pure" water. We also tested the resonator with a non-conducting liquid (cyclohexane).

Results and Future Plans: The data for $\varepsilon(T)$ were acquired between 1° C and 145° C. The data for two water samples differing in conductivity by a factor of 3.6 and for the two resonance frequencies differing by a factor of 2.6 were simultaneously fit by the polynomial function

$$\varepsilon(T) = 87.9144 - 0.404399\,t + 0.58726\times10^{-4}\,t^2 - 1.32802\times10^{-6}\,t^3$$

with a remarkably small residual standard deviation of 0.0055. The present results are a factor of five more precise than comparable measurements and we believe resolve the longstanding uncertainties concerning $\varepsilon(T)$ for pure water.

Publications:

Hamelin, J., Mehl, J.B., and Moldover, M.R., ***"The Static Dielectric Constant of Liquid Water between 274 K and 418 K near the Saturated Vapor Pressure,"*** Int. J. Thermophysics (in press).

Hamelin, J., Mehl, J.B., and Moldover, M.R., ***"Resonators for Accurate Dielectric Measurements in Conducting Liquids,"*** Rev. Sci. Instrum. 69, 255 (1998).

5. *Computational Chemistry Comparison and Benchmark Database*

R.D. Johnson III

Objective: 1) Provide a benchmark set of molecules and reactions for the evaluation of *ab initio* computational methods. 2) Provide users of computaitonal chemistry codes with the means to compare thermochemical property values predicted by different *ab initio* computational methods with experimentally determined values. This will also provide users of these methods with the means to evaluate the uncertainties in the computed thermochemical properties.

Problem: As computer power increases there is more reliance on modeling and computational chemistry in the chemical industry. This is due to the increased safety and speed, and decreased cost of models and calculations compared with laboratory measurements. This trend will continue as the computers and software become more powerful. *Ab initio* computational chemistry methods can provide accurate values for structures, entropies, and heats of formation. However the cost of the calculation increases greatly as the accuracy increases. The errors in the computational methods are systematic, depending on the computational method and functional groups that compose the molecule. In order to take advantage of the computational methods for thermochemical property estimation, accuracy and cost of need to be evaluated.

Approach: In order to facilitate testing we will provide a set of benchmark molecules and reactions with evaluated thermochemical data, giving both the value and its uncertainty. In addition, we will provide data from many levels of *ab initio* calculations for comparison with experiment. The goal is to have on the order of 500 species in the database for comparisons.

The presentation will be through a web interface where a user can select a subset of molecules from the database (such as all species containing Phosphorus), and the property to compare (such as heat of formation at 298.15K). The user will be presented the experimental and calculated values as a table or chart. By comparing the experimental and computed thermochemical values for a given set of molecules the systematic errors in the computed values can be determined.

Results and Plans: A set of over 600 species with well-known heats of formation has been assembled and will be accessible over the web. Tools are being developed for viewing and accessing this data, such as comparing experimental and theoretical heats of atomization, and comparing relative energies of isomers. Experimental data is being collected and evaluated. As well as heats of formation, we are adding structures, and ion properties, such as ionization energies, proton affinities, and electron affinities. The first release of the database is planned near the end of FY99. The completion of the calculations for all of the levels of theory is an ongoing activity.

6. *Critical Evaluation of Chemical Kinetics Data - New Solutions to Old Problems*

W. Tsang, R.F. Hampson, V.I. Babushok (Guest Researcher), W.G. Mallard, D.H. Frizzell, J.J. Reed, F. Westley (Contractor), Y.A. Mirokhin (Guest Researcher), J.T. Herron (Contractor), and C-Y Lin (Contractor)

Objectives: To collect and evaluate data on the rates of gas phase chemical reactions needed for modeling natural and industrial processes; to develop new calculational tools for evaluating data on pressure-dependent rate constants.

Problem: Understanding complex chemical processes – such as those that occur in the atmosphere, a furnace, or a chemical vapor deposition reactor – often requires a detailed model of the chemical changes that are occurring. To create such a model, one requires a rate for each reaction in the system, usually as a function of temperature. While much of this information exists, it is often fragmentary and difficult to find. In addition, older analyses of experiments have often proven to be incomplete and the resulting rate constants reported incorrect. In addition to the collection and evaluation of temperature-dependent rate constants, efforts are also needed to understand the dependence on pressure.

Approach: There are several components of this work. First, the technical literature is routinely searched and all publications presenting data on the rates of chemical reactions are retrieved, and data relevant to on-going evaluation projects are abstracted for use by evaluators. Second, the data are compared to other similar systems, and when possible, models of complex systems are developed and compared to experimental results. The resulting kinetic parameters are examined to determine trends in reactivity and associated bond energies implied by the kinetic parameters. Comparisons of these results with theoretical calculations are made. The results of these studies are published in the literature and distributed as electronic data sets. One of the most important methods of making the data available is via the Chemical Kinetics Database for use on personal computers.

Results and Future Plans: The Windows version of the Chemical Kinetics Database with over 9500 reactant pairs was released in November of 1998. The number of reaction rates in the database has increased from the prior release by about 50 %. In addition, a new set of tools for the analysis of complex unimolecular and recombination reactions has been developed. The analysis of data on these reactions has always been dependent on model calculations, the most common being the so-called RRKM model. The development of a detailed master-equation-based analysis of the thermal activation process of these complex systems has led to a better understanding of many recombination reactions for which there are multiple pathways. These reactions are especially difficult to model in cases in which radical recombination produces species that have sufficient energy to go into various other reactive channels as well as to return to the original products. The detailed solutions to these problems based on master equations have begun to yield predictive tools for these complex reactions. A long-range goal is to provide simple tools to allow the non-expert to perform pressure-dependent calculations easily, perhaps as part of a single, integrated package.

Publications:

Mallard, W.G., et al., ***"NIST Standard Reference Database 17: Chemical Kinetics, Version 2Q98,"*** National Institute of Standards and Technology, Standard Reference Data Program. Gaithersburg, MD (1998).

Tsang, W., Bedanov, V., and Zachariah, M.R., ***"Unimolecular Decomposition of Large Organic Radicals with Low Reaction Thresholds: Decomposition and Reversible Isomerization of n-Pentyl Radicals,"*** in Berichte der Busengesellschaft fur Physickalische Chemie (in press).

Babushok, V.I., Tsang, W., Burgess, D.R., and Zachariah, M.R., ***"Numerical Study of Low and High Temperature Silane Combustion,"*** Proceedings of the 27th Combustion Symposium (in press).

7. *Chemical Kinetics and Reaction Mechanisms of Hydrocarbon Radicals*

A. Fahr *and J.W. Hudgens*

Objective: To determine by a variety of experimental and theoretical methods the reaction rate coefficients and chemical mechanisms of hydrocarbon radicals, with an emphasis on unsaturated radicals.

Problem: Radical-radical and radical-molecule reactions involving hydrocarbon radicals are of considerable experimental, theoretical, and practical interest. Accurate determinations of relevant rate coefficients and reaction mechanisms are needed to produce predictive models of numerous macroscopic processes, e.g., incineration of polymers, high temperature combustion, soot formation, industrial halogenation, photochemistry of planetary atmospheres, and hydrocarbon oxidation occurring in the earth atmosphere.

In spite of their importance, few kinetic properties are known for unsaturated hydrocarbon radicals. Furthermore, the multitude of product channels available to these radicals can greatly complicate the interpretation of even the simplest kinetic experiment. Thus, accurate determinations of hydrocarbon radical kinetics present many research challenges.

Results and Future Plans: The investigations currently focus on the reactions of vinyl (C_2H_3), propargyl (C_3H_3), allyl (C_3H_5), ethynyl (C_2H), and methyl (CH_3) radicals and also upon the reaction of radicals produced during the chlorination of hydrocarbons. The spectroscopic and kinetic parameters are determined over temperatures from 300 K to 450 K and pressures from 250 Pa to 1100 Pa.

1. Photolytic Production and Reaction Kinetics of Propargyl (C_3H_3) Radical: During combustion, the self reactions of propargyl radicals lead to soot formation. Currently, a controversy exists over the magnitude of the self reaction rate coefficient that is appropriate for use in soot formation models. At NIST this reaction rate has been measured directly by cavity ring-down (CRD) spectroscopy and by kinetic absorption spectroscopy. Both studies used excimer laser photolysis to generate propargyl radicals. The two real-time absorption spectroscopic measurements found a rate constant of $(4.1\pm0.4)\times10^{-11}$ cm^3 molec^{-1} s^{-1}, which is a factor of 2.5 slower than reported previously. In addition, GC-MS analyses found that propargyl radical combination reactions produce three C_6H_6 isomers with 1,5-hexadiyne being the major product ($\approx$60 %) followed by 1,3-hexadiene-5-yne ($\approx$25 %) and a third isomer of C_6H_6 that has not yet been characterized. We have also studied propargyl-methyl cross-combination reactions and found a rate constant coefficient of $(1.5\pm0.6)\times10^{-10}$ cm^3 molec^{-1} s^{-1}. This cross-combination reaction produces two isomers of C_4H_6, 1-butyne and 1,3-butadiene.

2. Pressure Effect on Combination and Disproportionation of Radical-Radical Reactions: The effects of pressure on self reactions of vinyl (C_2H_3) and ethyl (C_2H_5) and cross-reactions of vinyl and methyl radicals were investigated in a pressure range of 300 Pa to 67 kPa. For vinyl-vinyl and vinyl-methyl reactions we found that the ratio of combination/disproportionation channels decreases significantly with decreasing pressure. No pressure effect on the ratio of combination/disproportionation of ethyl radical self reactions was observed. These findings are mechanistically very important and will have significant impact on the modeling of planetary atmospheres. We are now extending these studies to other radicals and attempting to establish a theoretical basis for our findings.

3. Ultraviolet Absorption Spectrum and Cross Sections of Vinyl (C_2H_3) Radical: Vinyl radicals were produced from excimer laser photolysis of various radical precursors and the absorption spectrum for the radical was obtained in the range of 220 nm to 250 nm. The observed spectrum exhibits a broad feature with a cross section of 5.3×10^{-18} cm^2 molec^{-1} at 230 nm. This absorption band could be used for direct kinetic studies of vinyl radical.

4. Photolytic Production and UV Absorption Detection of Ethynyl (C_2H) Radical: Many aspects of the electronic structure and spectrum of ethynyl remain uncertain and no gas phase absorption in the VUV-Vis region has been detected for this radical. We recently examined a few selected potential photolytic sources of ethynyl

radical and scanned a wide UV spectral range, from 230 nm to 260 nm, and searched for an electronic absorption of the radical. Gas chromatographic analysis of photolyzed samples showed diacetylene formation (the product of ethynyl combination reaction) as the major product. Also, a relatively broad absorption with medium intensity but with some structure was detected which we believe originated from the *X* - *B* electronic transition of C_2H. These studies are in progress and we plan to obtain the absorption cross section for the radical and use the absorption for direct kinetic studies.

5. Correlation Between Rate Constants and Energetics of Radical-Radical Reactions: In an effort to identify correlations between the rate of radical-radical combination reactions and physically meaningful parameters, reaction rates and energetics for a series of hydrocarbon radicals were examined. Radical-radical reactions occurring with very fast rate constants have, in addition to the usual singlet state product, a low lying and energetically accessible bound triplet state. Studies of this kind are very significant in establishing predictive methods that can be applied to similar reaction systems that are difficult to study experimentally. We hope to refine the theoretical aspects of our findings in the future.

6. Chlorination Reactions of Unsaturated Hydrocarbons: Industry uses chlorine addition reactions with hydrocarbons to produce a wide variety of compounds. However, the fundamental reaction mechanisms of these processes are poorly characterized and few rate coefficients are available to support computational models. Improved knowledge of the elementary reaction steps may facilitate process optimization, including the suppression of unwanted side reactions. We have used CRD spectroscopic detection and GC-MS analysis to investigate chlorination reactions of propargyl chloride. Chlorine atoms add to propargyl chloride and form two distinct vinylic isomers. The nascent vinylic radical formed by chlorine addition at the end-carbon decomposes to form a chlorine atom and a chloroallene molecule. The vinylic radical formed by chlorine addition onto the center carbon is relatively stable and is the dominant reaction intermediate that facilitates the synthesis of heavier chlorohydrocarbon molecules. These observations differ greatly from those predicted from thermodynamic considerations. Thermochemical models predict that both nascent, vinylic radicals isomerize into relatively stable, 1-chloro- and 2-chloro-allyl radicals. In contrast, the experimental data and *ab initio* calculations find that high energy barriers block all isomerization into allyl radicals. Thus, a completely different set of reaction products is produced.

8. Thermodynamics of Free Radicals in Aqueous Solutions

P. Neta, R.E. Huie, and T.N. Das (Bhabha Atomic Research Centre, Mumbai, India)

Objective: To obtain fundamental thermodynamic values for basic free radicals in aqueous solutions.

Problem: The thermochemistry of reactive, free radical intermediates is an important starting point in the understanding of most chemical processes. A reliable database on radical thermochemistry is of considerable importance: to industry, where the data are input for models used in the design of energy efficient processes that have minimal environmental impact; to physiological chemistry, where free radical thermodynamics underlies the understanding of deleterious oxidation processes; to environmental chemistry, where thermodynamics assists in the understanding of free radical degradation processes; to waste treatment, since free radical chemistry is central to all advanced oxidation processes; and to semiconductor fabrication, where ions and radicals modify surfaces. Indeed, just as the chemical thermodynamics of molecules has been the bedrock upon which our understanding of chemistry has been built, the chemical thermodynamics of free radicals is central to our understanding of chemical processes for the future.

Approach: Thermodynamic properties of free radicals in aqueous solutions are determined by the pulse radiolysis technique using the newly installed linear accelerator. The measurements involve determination of one-electron reduction potentials of unstable species through the rapid establishment of equilibria between the redox pair (e.g., radical/molecule) and a reference redox pair whose potential is well known. The pulse radiolysis technique permits production of various unstable radicals and monitoring of their redox equilibria before any significant decay of the radicals via other reactions. The equilibrium constant is determined either from the concentrations of the four components at equilibrium or from the rate constants for the forward and reverse reactions. From the known reduction potential of the reference redox pair one can determine the reduction potential of the investigated pair. These one-electron reduction potentials are not measurable by classical techniques because of the instability of the free radicals involved.

Results and Future Plans: The reduction potential for the tert-butylperoxyl radical/tert-butyl hydroperoxide was found to be $E(\text{t-BuOO}/t\text{-BuOO}^-) = 0.71$ V vs.NHE and $E(\text{t-BuOO}/t\text{-BuOOH}) = 1.05$ V at pH 7 and 1.47 V at pH 0. This is the first direct determination of a reduction potential for a peroxyl radical. From the value at pH 0, the O-H bond dissociation energy for t-BuOOH was estimated to be 369 kJ mol^{-1}. Values for other peroxyl radicals were estimated from kinetic correlations. Other measurements led to determination of reduction potentials for several phenoxyl type radicals derived from phenols, naphthols, and pyridols, and to the estimation of the O-H bond dissociation energies for these phenolic compounds. The values of the reduction potentials and bond energies are crucial for predicting the antioxidant power of such compounds in various media. Recently, the reduction potentials of the SO_3^- and SO_5^- radicals have been determined in order to provide essential information for modeling the reactions of such radicals in atmospheric droplets and in other autoxidation processes. Similar studies on the radical derived from thiosulfate indicate that it exists in the dimeric form, $S_4O_6^{3-}$, and its reduction potential was determined.

Another sulfur radical under study is that derived from sulfide, which can exist as the monomeric S^- or HS and the dimeric HSS^-. Other important inorganic radicals for which reduction potential information is lacking or incomplete include NH_2, N_2H_3, and SF_5 radicals and several metal ions in unstable oxidation states. The reactions of transition metal ions with free radicals often lead to intermediate complexes, which control the overall kinetics and final outcome of the process. The properties of representative species of this type will be examined.

Publications:

Das, T.N., Dhanasekaran, T., Alfassi, Z.P., and Neta, P., ***"Reduction Potential of the tert-Butylperoxyl Radical in Aqueous Solutions,"*** J. Phys. Chem. A 102, 280 (1998).

Das, T.N., and Neta, P., ***"Reduction Potentials of Naphthoxyl and Pyridoxyl Radicals in Aqueous Solutions,"*** J. Phys. Chem. A 102, 7081 (1998).

Das, T.N, Huie, R.E., and Neta. P., ***"Reduction Potentials of SO_3^-, SO_5^-, and $S_4O_6^{3-}$ Radicals in Aqueous Solutions,"*** J. Phys. Chem. (in press).

9. *Thermophysical Properties of Gases Used in Semiconductor Processing*

J.J. Hurly, K.A. Gillis, and M.R. Moldover

Objective: To provide industry with high-accuracy data for modeling CVD (chemical vapor deposition) processes and for calibration of MFCs (mass flow controllers) used in semiconductor processing.

Problem: Many process gases are toxic. and/or corrosive. and/or pyrophoric. For such gases, measurements of their thermophysical properties are sparse and rarely accurate. Accurate thermophysical property data are required to model the hydrodynamics of the gas streams, *i.e.,* the velocity and temperature profiles in the vicinity of the hot susceptor, together with the concentration and temperature gradients that evolve within the streams used in CVD processes. MFCs are used to deliver process gases (*e.g.*, Cl_2, HBr, BCl_3, WF_6) for CVD and other processes (*e.g.,* plasma etching) throughout the semiconductor industry. Calibrated MFCs are needed to scale processes up from prototype to pilot plant and to production. The operation of MFCs depends upon heat transfer through the process gas; however, MFCs are sold based on calibrations for benign "surrogate" gases such as N_2, CF_4, SF_6, and C_2F_6. Rationalization of this practice requires data for the density, heat capacity, thermal conductivity, and viscosity of the process gases as functions of temperature and pressure.

Approach: The Fluid Science Group is using acoustic techniques to measure the thermophysical properties of three classes of gases: (1) binary mixtures of CVD carrier gases with process gases, (2) pure process gases, and (3) surrogate gases. The Group will develop a comprehensive, reliable database for these gases that provides the heat capacity, thermal conductivity, viscosity, and the pressure-density-temperature relation for the gases and also diffusion coefficients for mixtures of the gases. The diffusion coefficients will be obtained from models for the intermolecular potentials between the carrier and the process gases.

Results and Future Plans: We have assembled and tested a facility in which acoustic techniques can be used safely for measuring the properties of these hard-to-handle gases. During the past year, we measured speed of sound in six of the gases that were identified by the SEMATECH MFC Working Group as having high priorities, namely, the process gases Cl_2, HBr, and BCl_3, and the surrogate gases CF_4, SF_6, and C_2F_6. The data range from somewhat below the boiling temperature to 200 C and from 25 kPa to 400 kPa or 80 % of the vapor pressure, whichever is lower. The data were analyzed for the ideal-gas heat capacity and the equations of state with uncertainties of approximately ±0.1 %. Effective pair potentials were derived from the data and used to estimate the transport properties of these gases. In the coming year, the data will be extended to higher temperatures (until chemical instability becomes a problem) and acoustic measurements of the transport properties will be performed. Also, additional gases will be studied.

Publications:

Hurly, J.J. ***"Thermophysical Properties of Gaseous CF_4 and C_2F_6 from Speed of Sound Measurements,"*** Int. J. Thermophysics (in press).

10. *Measuring and Modeling Solute-Solvent Interactions in Supercritical and Subcritical Fluids*

*T.J. **Bruno** and A.F. Lagalante*

Objective: To develop and test predictive models for solubilities of compounds in alternative solvents at supercritical, near-critical, and subcritical conditions using a combination of both physical and chemical variables as input into an empirical multivariate statistical model.

Problem: The most important piece of thermophysical data to assess the feasibility of an extraction process is the solute-solvent phase equilibrium. Serious limitations exist in equation-of-state modeling approaches that use only physical properties of the solute and solvent to model supercritical and near-critical solute solubility.

Approach: Safe replacements for conventional solvents are likely to come from fully or partially fluorinated alkanes, ethers, or ketones that possess negligible ozone depletion potential, as well as functionalized glycol ethers and siloxanes. Many of the fluorinated alternative solvents are gases under ambient conditions, and their thermophysical properties offer the promise of both conventional liquid extraction and the tunable solvent strength offered by near-critical and supercritical fluid extraction. In our approach, a given solution process is empirically modeled as the dependent variable in a multivariate statistical analysis. The independent variables to the multivariate statistical model include quantitative measurements of solute-solvent interactions and additional state-dependent terms. Solute-solvent interactions are quantified using the Kamlet-Taft (KT) solvatochromic chemical parameters. These parameters are empirically determined values of three solvent-solute interactions: acidity, basicity, and dipolarity-polarizability. The parameters are used in models to aid in the identification of alternative solvents by making it possible to predict the solubility of industrially relevant compounds.

Results and Future Plans: In recent years, we have designed and constructed numerous instruments for the quantitation of solubilities of solutes in sub- and supercritical fluids. Solutes studied have ranged from classes of organometallic compounds to physiologically active natural products. The KT parameters for the fluorinated ethane solvents have been measured using high-pressure equilibrium cells. Values are density-dependent over the gas-to-liquid density range. KT parameters for the glycol ethers and siloxanes have been measured for both the pure compounds and aqueous solutions of the compounds. We have measured water-solvent partition coefficients for sets of organic solutes in fluorinated ethane solvents. Based on the measured water-solvent partition coefficients and the measured KT values for the fluorinated ethanes, a model was developed to predict the solute partition coefficients in 1,1,1-trifluoroethane and 1,1,1,2-tetrafluoroethane, as well as in carbon dioxide. In the future, we will model other types of equilibria, such as solubility and gas chromatographic retention times in the alternative solvents, and characterize the interactions of modifiers in supercritical fluids. A predictive solubility model will suggest suitable alternative solvents and extraction conditions to substitute for an obsolete chlorinated solvent. The model will be tested using the pure fluorinated alternative solvents and we envision that the model can be applied to other classes of solvents as well as to azeotropic mixtures of solvents.

Publications:

Lagalante, A.F. and Bruno, T.J., ***"Modeling the Water-Supercritical CO_2 Partition Coefficients of Organic Solutes Using a Linear Solvation Energy Relationship,"*** J. Phys. Chem. 102, 907 (1998).

Lagalante, A.F., Hall, R.L, and Bruno, T.J., ***"Kamlet-Taft Solvatochromic Parameters for the Fluorinated Ethane Solvents,"*** J. Phys. Chem. B 102, 6601 (1998).

Lagalante, A.F., Wood, C., Clarke, A.M., and Bruno, T.J., ***"The Kamlet-Taft Solvatochromic Parameters for 25 Glycol Ether Solvents and Glycol Ether Aqueous Solutions,"*** J. Sol. Chem. 27, 887 (1998).

11. *Measurements and Data for Membrane Separations*

J. ***Pellegrino,*** *E.J. Han, G. Amy (Univ. Colorado), J. Cho (Univ. Colorado), M. Chapman Wilbert (U.S. Bureau of Reclamation), K. Price (U.S. Bureau of Reclamation), and S. Delagah (Univ. Colorado)*

Objective: To develop improved quantitative characterization techniques and predictive models for the filtration of complex mixtures using commercial membranes based on high quality measurements of streaming potential and water transport coefficients and detailed measurements of filtration results on dilute, complex aqueous mixtures encountered in membrane-based separations.

Problem: Since the first commercially-viable synthetic membranes suitable for molecular scale separations (reverse osmosis, nanofiltration, and ultrafiltration) were developed, over 25 years of research has still not produced a systematic approach for matching membranes to complex mixtures and predicting the filtration figures-of-merit: species partitioning into the membrane (rejection), solvent (water) permeability, and decline of permeability with time.

Approach: This program has both measurement and modeling components. Meaningful and accurate measurements on both the membrane and the complex mixtures are required to develop a systematic correlative approach. These measurements provide a means to evaluate the effects of chemical, physical, and structural characteristics of the membrane and the mixture, and ultimately, to delineate rational design criteria for separations. Through our collaborations with the U.S. Bureau of Reclamation and the University of Colorado, we are developing new test protocols, refining existing characterization techniques, and developing a database of consistently-obtained measurements of filtration figures-of-merit and membrane and mixture characteristics. This database is being compiled to facilitate the development of correlative models for matching membranes to specific applications. Improved processes for obtaining specialty chemicals, pharmaceuticals, and advanced monomers using environmentally benign processes, and more economical ways to recover, reuse, and supply water are examples of important industrial and municipal uses of membranes.

Results and Future Plans: This year we have successfully developed an improved protocol for measuring the tangential flow streaming potential of membrane sheets. This technique is commonly used to characterize the relative surface energy and charge at the membrane interface. The improved protocol is expected to increase the usefulness of this technique to monitor surface changes from both manufacturing recipes and end use. We also built and began testing a new apparatus to measure the kinetics of solvent diffusion through membranes. This apparatus has a resolution on the order of 10^{-8} L/s and may provide an improved method for absolute characterization of membrane materials and monitoring of very subtle structural changes from aging, exposure to chemicals, and mechanical trauma. Our database measurements have focused on the filtration of natural organic matter (NOM). NOM is a complex mixture of polycyclic, functionalized aromatic compounds with a relative molecular mass range from 400 to 5000. We have measured membrane properties (streaming potential, contact angle, water permeability, and partitioning of standard PEG mixtures); NOM solution properties (254 nm UV-VIS absorbance, concentration, conductivity, and the size exclusion chromatograph); and the filtration figures-of-merit. While continuing to add to this database we are now investigating a variety of semiempirical models for correlating the filtration performance with the membrane and mixture properties.

Publications:

Chapman Wilbert, M., Pellegrino, J., and Zydney, A., "***Bench-Scale Testing of Surfactant-Modified Reverse Osmosis/Nanofiltration Membranes,***" Desalination 115, 15 (1998).

Cho, J., Amy, G., and Pellegrino, J., ***"Membrane Filtration of Natural Organic Matter: Comparison of Rejection and Flux Decline Characteristics with UF and NF Membranes,"*** Water Res. (in press).

12. Phase Equilibria Measurements and Models for Hazardous Chemical and Mixed Waste Systems

C.D. Holcomb, L.A. Watts, S.L. Outcalt, W.M. Haynes, and B. Louie; M. Mullins, T.N. Rogers, and A.A. Kline (Michigan Technological University)

Objective: To develop and validate models that accurately predict the phase equilibria and thermodynamic properties of hazardous aqueous systems necessary for the safe handling and successful design of separation and treatment processes for these systems and to accurately measure the phase equilibria and thermodynamic properties of a representative system (water + acetone + isopropyl alcohol + sodium nitrate) over the applicable ranges of temperature, pressure, and composition.

Problem: Mixed hazardous and low-level radioactive wastes are in storage at DoE sites around the United States, awaiting treatment and disposal. These wastes contain many components in multiple phases, presenting very difficult handling and treatment problems. Current facilities do not have the capacity or technology to handle this waste (approximately 167,000 cubic meters), let alone the additional waste generated from continuing cleanup efforts. The safe handling, accurate characterization, and cost-effective design of new treatment techniques require an accurate and comprehensive knowledge of basic thermophysical property information. The complete modeling of mixed solvent electrolyte solutions is one of the remaining fundamental problems in solution thermodynamics. The lack of comprehensive and accurate predictive models for the properties of these systems represents a severe deficiency in the fundamental knowledge necessary to enable remediation efforts.

Approach: The model will use an equation of state to predict the vapor phase composition and density and to provide fugacity coefficients. The salt will be introduced into the equation of state through local composition based mixing rules. The model will form the basis for designing mixed waste separation and destruction processes for which no design data previously have been available. The model development requires volumetric data and phase compositions over a wide range of temperature and pressure. Measurements of the properties (phase equilibria, coexisting phase densities, and compressed liquid densities) for a representative waste system (water + acetone + isopropyl alcohol + sodium nitrate) will be acquired and used to develop and validate the models for these complex wastes. The data will cover the temperature range of 275 K to 425 K at pressures to 14 MPa and will be combined with well-documented chemical equilibrium data available in the literature.

Results and Future Plans: In the first year of this project, we have made significant progress in the database development, have begun testing the models, and have studied the pure components. An extensive literature search has been completed, and the data are being shared by NIST and Michigan Technological University (MTU). Data of the highest quality are being used to test the models for the system under study and to identify gaps in the data where our measurements should be concentrated.

Two models are being investigated by NIST and MTU. The NIST model concentrates on the phase equilibria and coexisting densities and the MTU model focuses on the liquid phase activities. The NIST model has been tested with saturation pressure data for the pure solvents (water, acetone, and isopropyl alcohol) and gives a relative deviation of less than 0.2 %. It has also been tested with a small amount of water + acetone data from the literature. The models are being evaluated with the preliminary database.

Calibrations and performance tests have been completed for the NIST apparatus. The ebulliometer at MTU is being modified and calibrated. Measurements of the vapor pressures and coexisting densities of water, acetone, and isopropyl alcohol are complete. In the next year of this project, the binary mixtures and ternary water + solvent mixtures will be studied and used to test the model. The binary liquid activity coefficients will be measured at MTU and tested with their model.

13. *Gas-Phase Thermochemistry of Iron Compounds*

C.B. Kellogg and K.K. Irikura

Objective: To predict and refine the heats of formation of a variety of iron compounds thought to participate in the chemical flame inhibition by iron pentacarbonyl.

Problem: In the search for non-ozone depleting halocarbon replacements, several metals, including iron, have been identified as super-efficient flame suppressants. Although some thermochemical data exist for the species that are thought to be most important in iron's flame chemistry, a more complete and accurate characterization of the thermochemistry of iron oxides, hydrides, and hydroxides is required to improve current kinetic flame models. Many of these species are transient and very difficult to characterize experimentally.

Approach: *Ab initio* investigations provide a straightforward means of acquiring accurate estimates of the thermochemical properties of the relevant iron compounds. However, transition metal compounds, especially those involving first-row transition metals, are notoriously difficult to characterize via *ab initio* methods. In recent years, however, density functional methods have emerged that can provide reasonable estimates of the structural and thermochemical properties of transition-metal-containing compounds. The B3LYP density functional was used to predict the geometrics and relative energeties of the lowest electronic states of the species of interest. The heats of formation were further refined by the results of more rigorous *ab initio* investigations employing coupled-cluster methods. The computational results were used in conjunction with model thermochemical reactions and available experimental data to predict the heats of formation of six iron compounds at 1500 K, a typical flame temperature.

Results and Future Plans: The investigations of iron thermochemistry isolated some species and reactions for which the existing experimental data conflict with computational predictions. The estimated uncertainty in the computational predictions indicates that they are more reliable than experiment for the heats of formation of several of the iron species. The results of the iron thermochemistry study are documented in a manuscript that has been submitted to the Journal of the American Chemical Society. Additionally, the results have been presented in a talk at the Fall National Meeting of the American Chemical Society. Work is currently underway to predict the thermochemistry of tin oxides and hydroxides in support of efforts to characterize the flame suppression mechanism of tin. In addition, work is underway to characterize the reaction barriers for a few of the key reactions in iron's flame chemistry. The current kinetic models assume that all reactions proceed without any barriers, but there is no direct evidence that this assumption is accurate.

Publications:

Kellogg, C.B., and Irikura, K.K., *"Gas-Phase Thermochemistry of Iron Oxides and Hydroxides: Portrait of a Super-Efficient Flame Suppressant,"* J. Am. Chem. Soc. (in press).

14. Thermophysical Properties of Natural Gas Systems

__R.A. Perkins,__ E.W. Lemmon, D.G. Friend, A.H. Harvey, C.D. Holcomb, M.L. Huber, A. Laesecke, J.W. Magee, M.O. McLinden, S.L. Outcalt, J.C. Rainwater, J.L. Scott, W.M. Haynes, I.M. Abdulagatov (Dagistan Scientific Center, Dagistan), and S. Kiselev (Inst. Oil and Gas Res., Russia)

Objective: To accurately measure the thermophysical properties of natural gas mixtures and to develop reference standard models that are internationally accepted for calculating properties within the required uncertainties of the data over large ranges of temperature, pressure, and composition.

Problem: The thermophysical properties of natural gas systems must be accurately known for national and international custody transfer. It is not possible to measure all possible compositions of natural gas, so accurate predictive models are required by industry. These models must be validated with reliable data obtained on a limited number of samples that have well defined compositions. The nature of custody transfer in gas pipelines and liquified natural gas shipping requires that these models be recognized as national and international standards.

Approach: The natural gas systems selected for experimental study are determined by comparisons of the best available models with existing data for systems that are of interest to industry. These comparisons identify systems where additional data are required to fill significant data gaps or where unresolved discrepancies exist between several data sets. Existing NIST models for natural gas mixtures, such as NIST Standard Reference Database 14, are based on one-fluid corresponding states and were developed for carbon-dioxide-rich systems. Improved Helmholtz energy formulations, which also allow calculation of all thermodynamic properties in the fluid phases of a mixture system in a consistent manner, offer potential for reduced uncertainty for a wider range of mixture systems. Experimental data obtained at NIST on gravimetrically prepared mixtures will extend and enhance the data available in the literature to develop accurate mixture models and to validate the performance of new mixture models.

Results and Future Plans: Measurements were reported for the molar heat capacity at constant volume for n-butane and isobutane from 141 K to 342 K for pressures up to 33 MPa. Measurements have been carried out for the molar heat capacity and density of 2 mixtures of propane and isobutane from 200 K to 400 K with pressures up to 35 MPa. Vapor-liquid equilibrium (VLE) and coexisting phase density measurements have been completed on the propane/isobutane system from 250 K to 395 K. Measurements of the density of 3 mixtures of carbon dioxide and ethane are being completed. Saturation heat capacity data for the light n-alkanes have been used to calculate the vapor pressure for these fluids at low reduced temperatures where no data were available. In conjunction with collaborators from Germany, new thermodynamic formulations for ethane and propane will be developed based on a structural optimization algorithm. Equations for calculating the vapor pressures and critical temperature and pressure of all normal alkanes and their isomers have been developed. A mixture model, based on a generalized corresponding-states algorithm for the excess Helmholtz energy and reference quality formulations for the constituents, has been developed. Future plans involve the addition of other fluids such as the heavier hydrocarbons, helium, hydrogen, water, carbon monoxide, and hydrogen sulfide.

Publications:

Lemmon, E.W. and Jacobsen, R.T, ***"A Generalized Model for the Thermodynamic Properties of Mixtures,"*** Int. J. Thermophys. (in press).

Magee, J.W. and Lüddecke, T.O.D., ***"Molar Heat Capacity at Constant Volume for n-Butane at Temperatures from 141 to 342 K at Pressures to 33 MPa,"*** Int. J. Thermophys. 19, 129 (1998).

15. *Database for the Chromatographic Analysis of Natural Gas*

T.J. Bruno

Objective: To provide an efficient, fast, and reliable method for identifying, in both the laboratory and the field, the heavier components of natural gas (the C_6+ fraction, that is, species that have a carbon number in excess of 6) and natural gas treatment materials.

Problem: The design of many processes involving natural gas, as well as the custody transfer of natural gas, rely on an accurate chemical analysis of the gas composition. For example, calorific value of natural gas is calculated from a chromatographic analysis of each individual gas stream. The most common analysis of natural gas at present considers only the lightest components. The heavier compounds are backflushed out of the column and through the detector as a single peak. This approach introduces significant uncertainty to subsequent calculations based on the gas composition. The inclusion of the heavier fraction into the analysis (an approach called the "extended natural gas analysis") is a complex problem. In particular, natural gas consists of upwards of 400 organic and inorganic constituents, most of which occur naturally, and some of which are introduced intentionally during processing. Moreover, the composition varies with season, with source-well long-term history, and with short-term usage and storage history. Thus, a fast, low-cost, and reliable method is required for the efficient commerce and use of this vital natural resource.

Approach: Gas chromatography offers an economical and accurate solution to the problem of the extended natural gas analysis. In addition to being one of the most well understood and economical analytical methods available, it is very amenable to field applications. What is needed is an interactive database that can be incorporated into the control and analysis software of both laboratory and field gas chromatographic instrumentation. We have approached the problem of standardizing and automating the extended natural gas analysis through the measurement of standard chromatographic retention parameters on the most useful stationary phases available, and also on some novel developmental phases. The standard retention parameters that we have measured include net retention volumes, relative retentions, and Kovats retention indices. These parameters are corrected for instrumental variation and are, therefore, reproducible from instrument to instrument. The measurements are performed on a specially modified commercial gas chromatograph that provides highly accurate retention information. The column temperature dependence of each retention parameter is modeled with appropriate equations to allow predictions at all relevant temperatures. These models then form the heart of an interactive database that allows offline identification of peaks, and also the optimization of more complex analyses.

Results and Future Plans: The measurement of all standard retention parameters at four or more column temperatures has been completed for a series of representative C_6+ hydrocarbons on eight stationary phases. In addition, similar measurements have been completed for 23 odorants on the same phases. These stationary phases include the well-known methyl silicones and their more useful derivatives, porous polymer and solid adsorbent SCOT (surface coated open tubular) columns, and also some novel stationary phases that include sol/gel phases and clay phases. During the next year, we will complete the final versions of the databases (the hydrocarbon and odorant editions) with all stationary phases.

Publications:

Bruno, T.J. and Wertz, K.H., ***"Gas Chromatographic Retention Parameters: The Basis of Chromatographic Peak Identification for Extended Natural Gas Analysis,"*** Proc. Institute of Gas Technology Symposium on Natural Gas Quality, Orlando, FL (1997).

16. Thermophysical Properties of Alternative Refrigerants

__M.O. McLinden,__ T.J. Bruno, C.D. Holcomb, M.L. Huber, A.R. Laesecke, E.W. Lemmon, J.W. Magee, S.L. Outcalt, R.A. Perkins, A.P. Peskin (High Performance Systems and Services Division, ITL), and L.A. Weber (Contractor)

Objective: To provide industry with high-accuracy property data and models for alternative refrigerants and refrigerant mixtures.

Problem: The CFC and HCFC refrigerants must be replaced with fluids that do not deplete stratospheric ozone. To evaluate the energy efficiency, capacity, etc. of any fluid in a thermodynamic cycle, or to design equipment using a new fluid, knowledge of the thermophysical properties is required.

Approach: Our work on alternative refrigerants represents a comprehensive approach to a major problem and has been supported by multiple government agencies and industry groups. The Division's work in this area includes experimental measurements and the compilation and evaluation of literature data. These data provide the input for developing the models that form the basis of the REFPROP database.

Results and Future Plans: A complete revision of the REFPROP database has been released. This database calculates the thermodynamic and transport properties for a wide variety of fluids and fluid mixtures being investigated for use in refrigeration equipment. It combines Fortran-based subroutines implementing a variety of fluid property models with a modern graphical user interface (GUI) written in Pascal. Mixture properties are calculated with a new model applying mixing rules to the Helmholtz energy of the constituent pure fluids. Included in this effort was the fitting of the mixture parameters to comprehensive data previously measured by NIST on a wide variety of refrigerant mixtures. We have also developed a predictive scheme to estimate, in the absence of data, the parameters in the mixture model.

The work on alternative refrigerants is shifting increasingly to mixtures and to the transport properties. We have completed thermal conductivity measurements on eight binary and two ternary mixtures of R-32, R-125, R-134a, and propane. In a comparison of recent viscosity measurements on these same ten mixtures, the modification to the extended corresponding states (ECS) model developed in 1998 was shown to be a significant improvement over earlier models.

We are now beginning to investigate the properties of refrigerant/lubricant mixtures. (The compressor in a refrigeration system utilizes a lubricant which subsequently circulates with the refrigerant around the entire cycle.) This work includes measurements of the density and surface tension of refrigerant/lubricant mixtures and the modeling of their properties using a SAFT (statistical associating fluid theory) approach. A new method, utilizing fluorescence spectra, has been developed to measure the amount of lubricant on a surface; it is applicable at lubricant concentrations as low as 5 ppm, μg/g.

Annex 18 of the International Energy Agency, an activity initiated and led by NIST since 1990, held its final meeting in Trondheim, Norway. In the last of a series of equation of state comparisons, the high-accuracy equation developed at NIST for R143a was declared the international standard for this fluid. Under the auspices of the IUPAC Subcommittee on Thermophysical Properties, NIST acts as one of three coordinators of a project on "Thermochemical, Thermodynamic and Transport Properties of Halogenated Organic Compounds and Mixtures."

Publications:

Lemmon, E.W. and Jacobsen, R.T, ***"Thermodynamic Properties of Mixtures of Refrigerants R-32, R-125, R-134a, and R-152a,"*** Int. J. Thermophysics (in press).

McLinden, M.O., Klein, S.A., Lemmon, E.W., and Peskin, A.P., ***"NIST Standard Reference Database 23: REFPROP, Version 6.0,"*** National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg, MD (1998).

17. *Thermophysical Properties of Ammonia-Water Mixtures for Use in Power Cycles*

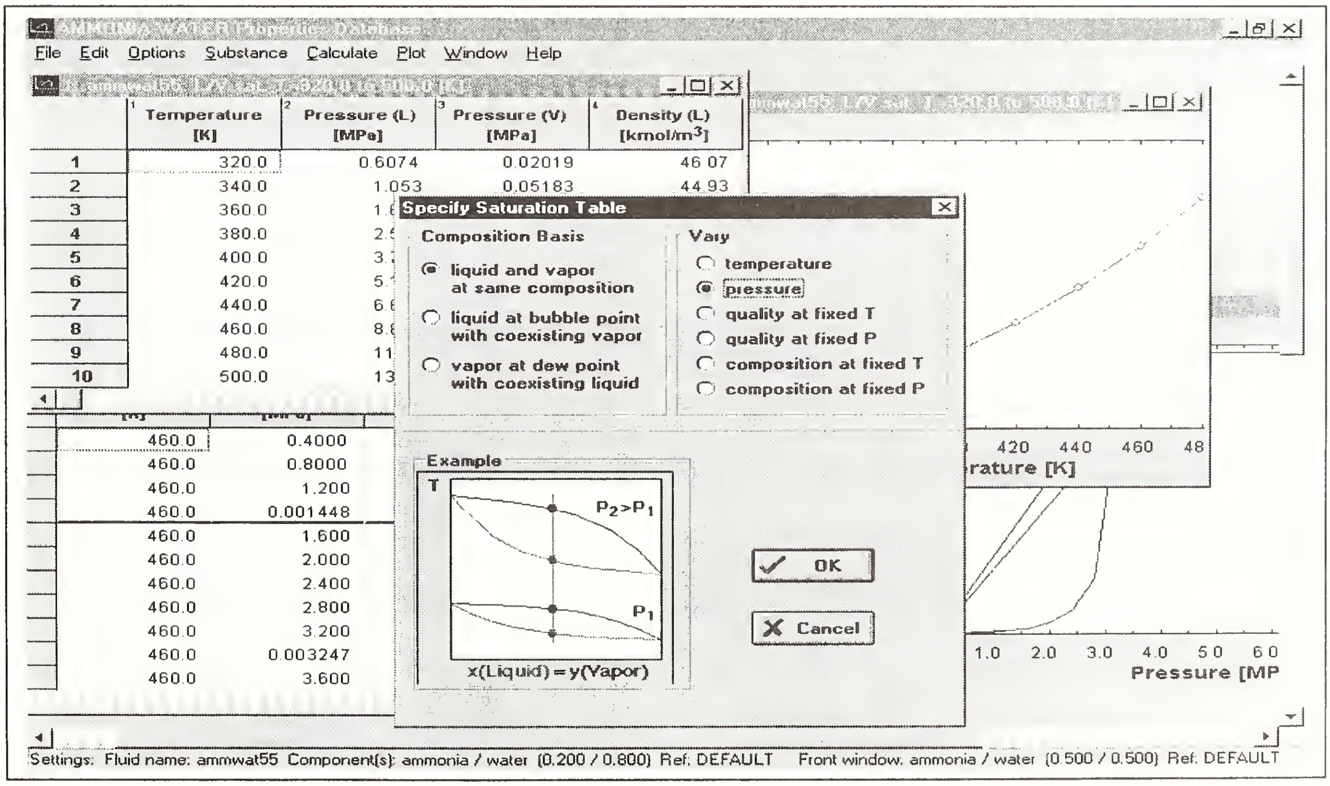
D.G. Friend, *J.C.Rainwater, C.D. Holcomb, J.W. Magee, R.A. Perkins, T. Lüddecke (Univ. Hannover, Germany), and S. Kiselev (Inst. Oil and Gas Res., Russia)*

Objective: To establish standard reference thermophysical property surfaces for mixtures of ammonia and water over broad ranges of temperature, pressure, and composition.

Problem: Drastically redesigned power plants have been proposed which use the binary ammonia-water system as a working fluid, and dramatic increases in efficiency have been predicted. Several companies have obtained license agreements to implement this approach. Critical design decisions and corporate risk analysis require property parameters which are not currently available. In addition to these engineering and other practical concerns, problems in the optimization of these new cycles and in the development of performance warranty protocols have not been resolved because of uncertainties in the properties of the working fluid. This binary system is also the working fluid in some refrigeration applications, including prospective domestic heat-pump and air-conditioning technologies; the optimization of designs for these systems also requires reliable standard property information.

Approach: The project has included an extensive effort of bibliographic study and evaluation of existing data; details concerning the required data and tolerances for industrial application are also needed. Experimental measurements are needed for selected properties at the most important state points; these include measurements of the Vapor-Liquid Equilibrium (VLE) surface, density, isochoric heat capacity, thermal conductivity, and viscosity. Some apparatus modification and development are required to perform the measurements. The modeling effort includes studies based on scaling theory to describe the high pressure region of the phase boundaries, as well as several versions based on an extended corresponding states algorithm and a two-fluid Helmholtz energy model.

Results and Future Plans: The precise needs of industry were established through a workshop at NIST in 1996. Existing data have been collected and evaluated and the two-fluid model has been completed. A computer package for ammonia/water properties based on this information is nearing completion. Skeleton measurements of the isochoric heat capacity, the VLE surface, and pure ammonia



	1 Temperature [K]	2 Pressure (L) [MPa]	3 Pressure (V) [MPa]	4 Density (L) [kmol/m³]
1	320.0	0.6074	0.02019	46 07
2	340.0	1.053	0.05183	44.93
3	360.0	1.6		
4	380.0	2.5		
5	400 0	3.7		
6	420.0	5.1		
7	440.0	6.6		
8	460.0	8.8		
9	480.0	11		
10	500.0	13		

460.0	0.4000
460.0	0.8000
460.0	1.200
460.0	0.001448
460.0	1.600
460.0	2.000
460.0	2.400
460.0	2.800
460.0	3.200
460.0	0.003247
460.0	3.600

Specify Saturation Table

Composition Basis
- ● liquid and vapor at same composition
- ○ liquid at bubble point with coexisting vapor
- ○ vapor at dew point with coexisting liquid

Vary
- ○ temperature
- ● pressure
- ○ quality at fixed T
- ○ quality at fixed P
- ○ composition at fixed T
- ○ composition at fixed P

Settings: Fluid name: ammwat55 Component(s): ammonia / water (0.200 / 0.800) Ref: DEFAULT Front window: ammonia / water (0.500 / 0.500) Ref: DEFAULT viscosity have been completed. Comparisons with the models indicate that further refinement of the models may be required at higher temperatures and pressures. Work will continue on transport property measurements and analysis.

Publications:

Tillner-Roth, R. and Friend, D.G., "***Survey and Assessment of Available Measurements of Thermodynamic Properties of the Mixture (Water + Ammonia),***" J. Phys. Chem. Ref. Data 27, 45 (1998).

Tillner-Roth, R. and Friend, D.G., "***A Helmholtz Free Energy Formulation of the Thermodynamic Properties of the Mixture (Water + Ammonia),***" J. Phys. Chem. Ref. Data 27, 63 (1998).

Magee, J.W. and Kagawa, N., "***Specific Heat Capacity at Constant Volume for*** $\{xNH_3 + (1-x)H_2O\}$ ***at Temperatures from 300 to 520 K and Pressures to 20 MPa,***" J. Chem. Eng. Data 43, 1082, (1998).

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18. *Development of Apparatus to Measure Thermophysical Properties of Fluids*

R.A. Perkins, *W.M. Haynes, T. Bruno, B. Hansen (Contractor), C.D. Holcomb, L.A. Watts, A. Laesecke, J.W. Magee, M.O. McLinden, C. Muzny, S.L. Outcalt, J.L. Scott, and G.C. Straty (Contractor)*

Objective: To develop state-of-the-art experimental apparatus that are used to measure the thermophysical properties of a wide range of pure fluids and fluid mixtures important to the energy, chemical, and related industries with a high accuracy over a wide range of conditions.

Problem: The tools required to measure the thermophysical properties of fluids accurately over a wide range of conditions are not commercially available. The apparatus developed here are essential for the acquisition of high-quality data for key materials and industries, for the evaluation of scientific theories, and for the development of reliable methods to predict properties when data do not exist or would be difficult or impractical to obtain. They will advance the body of measurement technologies and data underlying current engineering practice and broaden the technical and conceptual base needed to solve the problems of the future.

Approach: The Experimental Properties of Fluids Group maintains a wide range of experimental apparatus to support the acquisition of accurate data on the thermophysical properties of fluids at temperatures from 30 K to 700 K with pressures to 70 MPa. This capability has been developed with the long-term support of the U.S. Department of Energy, Office of Basic Energy Sciences. New apparatus are developed based on the data required to address key industrial and governmental needs such as improved energy efficiency, custody transfer of natural gas, and the replacement of chlorofluorcarbons (CFC's). New measurement technology that is developed to meet these needs for thermophysical property data is available for application by industry while the apparatus themselves form a resource that is available for the study of pure fluids and fluid mixtures at NIST.

Results and Future Plans: Features that are common to all new apparatus are corrosion resistant construction, a high degree of computer automation, and small sample volumes. Small sample volumes reduce the hazards associated with toxic or otherwise hazardous fluids, reduce problems in obtaining research-grade samples, and shorten sample equilibration times. The instruments that are currently being developed include: phase-equilibria apparatus for azeotropic aqueous-organic-salt mixtures, light scattering apparatus to measure thermal diffusivity, small-volume dual-cell dew-bubble point apparatus, heat of vaporization calorimeter and effusion cell for vapor-pressure determinations, and solubility measurement apparatus using magnetic levitation. These apparatus significantly enhance our existing measurement capability for the study of the thermophysical properties of fluids and fluid mixtures and will become available for routine measurements in the coming year. Based on current and anticipated research needs, potential enhancements to our measurement capability have been identified and new apparatus will be developed as resources become available.

Publications:

Holcomb, C.D., ***"Design of a Vapor-Liquid Equilibrium, Surface Tension, and Density Apparatus,"*** Proc. 13th Symposium on Energy Engineering Sciences, Argonne, IL (in press).

Magee, J.W., Deal, R.J., and Blanco, J.C., ***"High-Temperature Adiabatic Calorimeter for Constant-Volume Heat Capacity Measurements of Compressed Gases and Liquids,"*** J. Res. NIST 103, 63 (1998).

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19. "Short-Lived Ozone-Related Compounds": A Chapter in the 1998 International Scientific Assessment of Ozone Depletion

M. J. Kurylo

Objective: To summarize the current scientific understanding of the atmospheric abundances of ozone and climate-related trace gases that have significant chemical or physical removal occurring in the troposphere.

Purpose: The 1998 Scientific Assessment of Ozone Depletion is the fourth international assessment report dealing with the science of ozone depletion. It has been prepared to assist the Parties to the United Nations Montreal Protocol in making decisions regarding the protection of the stratospheric ozone layer. The Montreal Protocol on Substances that Deplete the Ozone Layer states (Article 6) "...the Parties shall assess the control measures...on the basis of available scientific, environmental, technical, and economic information." To provide the mechanism whereby these assessments are conducted, the Protocol further states: "...the Parties shall convene appropriate panels of experts" and "the panels will report their conclusions...to the Parties." The 1989, 1991, 1994 and 1998 science assessments were conducted (in response to these Protocol requirements) under the auspices of the World Meteorological Organization, (WMO) and the United Nations Environment Programme, (UNEP) .

The 1998 Assessment consists of 12 chapters covering a broad range of topics that describe the state of scientific understanding of atmospheric ozone. Chapter 2 ("Short-Lived Ozone-Related Compounds") is one of two chapters explicitly treating the abundances, trends, sources, sinks, and lifetimes of important ozone- and climate-related trace gases. Lead-authorship responsibilities for this chapter were shared by Dr. Kurylo and Dr. Jose Rodriguez (Atmospheric and Environmental Research, Inc.). More than 30 co-authors and contributors from seven different countries participated in drafting the various sections that comprise the nearly 100 pages of chapter text, tables, and figures.

The primary focus of the chapter is on chlorine, bromine, and iodine containing organic compounds of both natural and anthropogenic origin that undergo significant removal in the troposphere. These include methyl chloride, bromide, and iodide; methyl chloroform; and a variety of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) now produced as substitutes for the regulated chlorofluorocarbons (CFCs). Nevertheless, the chapter also summarizes similar information for methane and carbon monoxide as well as several chemicals produced as products of the tropospheric degradation of HCFCs and HFCs. A parallel chapter (Chapter 1) covers the same issues for long-lived ozone-related compounds such as the CFCs, perfluorocarbons, and halons.

All chapters in the 1998 Assessment were reviewed in their draft forms in November 1997 by a panel consisting of the Assessment Co-Chairs, the chapter lead-authors, and several external atmospheric scientists. The revised chapters subsequently underwent international mail peer review during April and May 1998 by at least ten scientists per chapter. Finally, in June 1998 the lead chapter authors summarized their chapters (including their address of issues raised during the peer review) before an international panel of atmospheric scientists in Switzerland. This last review provided the basis for finalizing the chapters. Only scientific material that was supported by peer reviewed publications was allowed to be included in the final revisions. The assessment chapters thus reflect the state of knowledge as supported by completed science rather than by science in progress. Nevertheless, a considerable amount of research is still required and, in fact, is underway in many of the topical areas addressed.

The entire Assessment is now undergoing technical editing in preparation for its submission to WMO and UNEP in November 1998 and subsequent publication as a WMO Special Report in early 1999. A summary of the scientific highlights from the various chapters will be presented by the Assessment Co-Chairs at the next meeting of The Parties in Cairo, Egypt in mid-November, 1998.

Publications:

Kurylo, M.J., Rodriguez, J.M., Andreae, M.O., Atlas, E.L., Blake, D.R., Butler, J.H., Lal, S., Lary, D.J., Midgley, P.M., Montzka, S.A., Novelli, P.C., Reeves, C.E., Simmonds, P.G., Steele, L.P., Sturges, W.T., Weiss, R.F., and Yokouichi, Y., ***"Short-Lived Ozone-Related Compounds,"*** Scientific Assessment of the Ozone Layer: 1998, World Meteorological Organization, Global Ozone Research and Monitoring Project Report No. 44, Chapter 2.

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20. *Thermodynamic Data for Environmental Fate and Risk Analysis*

D.G. Archer, *M.W. Chase, D.R. Kirklin, R.D. Levin, and P.A.G. O'Hare*

Objective: To provide thermodynamic information necessary for prediction of movement of heavy metals through ground waters (aquifers) and surface waters, and for prediction of remediation yields in treatment methodologies.

Problem: The environmental fate of a heavy-metal contaminant in an aqueous environment is determined by the extent of many competing reactions. The competing reactions include precipitation reactions, reduction-oxidation reactions, and ion-exchange reactions with the geological materials present. The extent of reaction for these types of processes is determined by the thermodynamic properties for the reaction in the aqueous system. This is particularly true for movement of contaminants in aqueous environments because known diffusion laws predict mass flux to be dependent on concentration gradients. Prediction of the level of contamination of aquifers and surface waters, as well as the prediction of the rate of migration of contaminants through these waters, is accomplished through calculational models (simulators). Therefore, the validity of any particular simulator's calculated distribution of a noxious contaminant is heavily dependent on the validity of the thermodynamic information for the competing reactions that have been incorporated into the simulator. However, much of the thermodynamic information required to execute these calculations is not of sufficient accuracy to make the calculations meaningful.

Approach: We intend to generate accurate thermodynamic properties of heavy-metal containing species and the common ions with which these species come into contact. Examination of the status of the literature regarding these species will be conducted. These examinations will identify the relevant measurements described in the literature as well as document previous NIST tabulations of thermodynamic properties for these chemical species. From these analyses, the measurements necessary to determine accurately the thermodynamic properties will be identified and conducted. A data-handling structure will be constructed that allows simultaneous evaluation of thermodynamically consistent properties for the desired species.

Results and Future Plans: Protocol development for operation of the adiabatic solution calorimeter in the near-ambient temperature range was completed this year. Enthalpy of solution measurements for aqueous sodium chloride were performed with this instrument. These high-accuracy measurements establish sodium chloride as a calorimetric standard for enthalpy of solution calorimeters and demonstrate the calorimeter as the most accurate such calorimeter operating today. An equation of state for $MgSO_4 + H_2O$ was prepared and published. An analysis of the state of the literature for thermodynamic properties of common species of cadmium was published. During the next year, analyses of the literature on the thermodynamic properties of common species containing mercury, chromium, lead, zinc, manganese, and nickel, similar to that for cadmium, will be completed and published. Measurements for selected species will be initiated. Also expected is initiation of a program to determine accurate thermodynamic properties of "key" substances. The "key" substances are required to extract the properties of a heavy-metal containing reactant from the measured properties of a reaction.

Publications:

Archer D.G. ***"Thermodynamic Properties of Import to Environmental Processes and Remediation. I. Previous Thermodynamic Property Values for Cadmium and Some of Its Compounds,"*** J. Phys. Chem. Ref. Data 27, 915 (1998).

Archer, D.G. and Rard, J.A. ***"Isopiestic Investigation of the Osmotic and Activity Coefficients of Aqueous $MgSO_4$ and the Solubility of $MgSO_4 7 H_2O$ (cr) at 298.15 K: Thermodynamic Properties of the $MgSO_4 + H_2O$ System to 440 K,"*** J. Chem. Eng. Data 43, 791 (1998).

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21. The NIST Mass Spectral Database – Extending the Evaluation

S.E. Stein, *A. Mikaya (Contractor), Zhu Damo (Guest Researcher), D. Tchekhovskoi (Contractor), C.L. Clifton, and W.G. Mallard*

Objective: To provide the mass spectral community with a fully evaluated mass spectral database and with tested and documented search algorithms that will enable the positive identification of unknown organic compounds using gas chromatography/mass spectrometry (GC/MS).

Problem: Modern organic analytical chemistry is critically dependent on instrumental analysis. For qualitative analysis, there is no better tool than the mass spectrometer. Like many other analytical techniques, it is best used with a library of reference spectra. Even with good reference spectra, the data must be processed correctly. Robust algorithms that have been thoroughly tested to eliminate flaws are needed.

Approach: The new release of the NIST mass spectral data base – NIST 98 – provides a fully evaluated database of mass spectra with 129,136 evaluated spectra for 107,886 compounds. Structures are provided for 107,829 compounds, replicate spectra for 13,205 compounds. The data are largely for full spectra with a mean of 93 peaks/spectrum and a median of 78 peaks/spectrum. Each of these spectra has been looked at by at least one expert, and all questionable data by two experts. NIST 98 represents the very best collection of mass spectral data ever assembled. In addition over the last few years a number of advances in the algorithms for searching the database have been developed and extensively tested, both for their inherent functionality and to compare them to other search algorithms. The best algorithms are then incorporated into the NIST search software.

Results and Future Plans: The release of NIST 98 is a major milestone, it represents the work of 12 staff years by a number of mass spectrometrists. This effort is the first time such a large collection of scientific data from so diverse a set of experimenters has ever been evaluated. The data were examined for reasonable neutral losses, for air peaks, for impurities (either solvent or other related compounds), and for errors in transcription of the data from the original source. In every case where a change had to be made, agreement between at least two evaluators was required. The analysis was always conservative; if a given spectrum or spectral feature was not clearly in error, it was not changed. On the other hand, when the data were so suspect that they were impossible to repair, they were removed from the database. In some cases where there was no alternative spectrum, this meant that the compound itself was removed from the database. The decision was made to emphasize the quality of the final database and not the sheer size of the database. The resulting database represents the very best collection of mass spectral data ever assembled. The next step of the process is to extend the data evaluation into new data being added and to begin work on more detailed comparisons of related data. Additional work is being undertaken to provide computer based tools to aid in the evaluation as well as to provide users of the NIST software with tools for analyzing spectra from compounds which are not in the database.

In order to make the database more useful to the gas chromatography / mass spectral community, work has started on the addition of retention indices to the database. The retention index is a measure of the time it takes a compound to elute from the gas chromatography column. For many compounds which might otherwise be confused just using the mass spectrum, the retention index makes it possible for a more definitive positive identification to be made. An example of an important class of compounds for which the retention time data are especially useful is the hydrocarbons, many of which have very similar mass spectra. The first stages of compiling and entering the data has begun. Tools are being developed both to evaluate the data and to use the data for prediction of retention data for compounds for which data are not available.

Publications:
Ausloos, P., Clifton, C., Lias, S.G., Mikaya, A., Sparkman, O.D., Stein, S.E., Tchekhovskoi, D., Zaikin, V., and Zhu, D., ***"The Critical Evaluation of a Comprehensive Mass Spectral Library,"*** J. Amer. Mass. Spect. (in press).

Databases:
Stein, S.E., Fateev, O.V. , Tchekhovskoi, D., Zaikin, V., Zhu, D, Mikaya, A., Sparkman, O.D. Ausloos, P., Clifton, C., Lias, S.G., Levitsky, A., and Mallard, W.G., "NIST Standard Reference Database 1: NIST/NIH/EPA Mass Spectral Database - NIST 98," NIST Standard Reference Data Program, Gaithersburg, MD (1998).

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22. Automated Gas Chromatography/ Mass Spectral Decomposition and Analysis – Tools for Automating and Improving the Use of GC/MS Instruments

S.E. Stein*, O. Toropov (Contractor), A. Rumiantsev (Contractor), W.G. Mallard, and J.J. Reed*

Objective: To develop and test algorithms for automatically deconvoluting and analyzing GC/MS data files using a target library of compounds.

Problem: The program currently underway has been fully funded by the Defense Special Weapons Agency (DSWA) to provide a method for analyzing for chemical weapons banned under the Chemical Weapons Convention. The software implementing the algorithms must provide full blinding of the analysis process so as not to compromise the proprietary data of treaty participants. In general, the analysis of GC/MS data files for complex mixtures can be time consuming and error prone. The normal method of doing a background subtraction to extract the single component can be essentially impossible in a complex mixture because there is no background. Even in only moderately complex chromatograms, a manual subtraction can produce seriously erroneous results.

Approach: A detailed noise analysis is performed, followed by a deconvolution of each of the peaks in the total ion chromatogram based on the individual ion chromatograms. The resulting eluents are then compared to reference spectra using a series of algorithms that take into account the degree of confidence that an analyst would have in the deconvoluted peak. The identification is presented with a confidence measure. The process of extracting the distinct eluents (or components) out of a complex data file breaks down into four parts: noise perception and evaluation, component perception, signal extraction, and compound identification. The noise perception and evaluation is central to the analysis since the recognition of the difference between a "real" peak, caused by a compound eluting from the column, and a "false" peak, caused by noise, depends upon a knowledge of the nature and size of the noise. Once the noise is understood, the individual components can be extracted. The extraction of the signal involves examining the overlap of components and removing mass spectral peaks associated with a different eluent.

Results and Future Plans: The algorithm has been tested extensively using a target library of chemical weapons agents. Over 40,000 data files have been examined to ensure that the algorithm does not produce false positives. At the same time, a number of experiments have been performed with low concentrations of target compounds similar to chemical agents to demonstrate that the algorithm is sensitive enough to detect all true positives at analytically useful concentrations. The results of these tests have shown that the algorithms used in the development of the software are robust and capable of automated and blinded analysis. Work is continuing on refining the algorithms to reduce the incidence of false identifications by making use of data other than the mass spectra. The use of retention indices is central to the further reduction of false positives. The software developed here has been adapted by the Organization for the Prohibition of Chemical Weapons (OPCW) for use in all inspections involving GC/MS instrumentation. Ongoing work to improve the algorithms is driven by the result of the analysis of this extensive set of data files as well as data taken specifically to provide difficult problems.

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23. *Evanescent Wave Cavity Ring-Down Spectroscopy: A New Tool for Studying Chemical Reactions at Interfaces*

A.C.R. Pipino

Objective: To significantly advance chemical kinetics metrology at interfaces and to provide fundamental kinetic data and mechanistic information related to important processes that occur at interfaces.

Problem: Chemical and physical processes occurring at interfaces are important in many industrial, environmental, and biological systems. To elucidate these interactions, spectroscopic techniques that provide identification and quantification of interfacial species with high sensitivity are needed. Although the study of surface chemistry has been an very active area of research for many years, the vast majority of the effort has focused on solid surfaces in vacuum, where electron spectroscopies provide sub-monolayer sensitivity. However, most real-world interfacial interactions occur at boundaries between two dense phases where there is a paucity of diagnostic tools. Techniques such as surface-enhanced Raman scattering and infrared reflectance have provided significant insight, but typically provide high-sensitivity only on specific metallic surfaces. Nonlinear optical techniques have also been very effective for interfacial diagnostics, but require high-peak-power pulsed lasers and frequently lack sensitivity at sub-monolayer coverage . Diagnostic tools are needed that can provide data at sub-monolayer coverage. For example, heterogeneous catalysts can be "poisoned" by less than 1/10 of a monolayer of a contaminant. To elucidate the poisoning mechanism, sensitive detection of reactive intermediates is required. Another important area of research requiring advanced interfacial diagnostics is the development of surface active chemical sensors. In addition, heterogeneous processes in the atmosphere, such as halogen activation on aerosols, are linked to ozone depletion. More accurate measurements of reaction rates at the relevant interfaces will improve the accuracy of environmental models.

Approach: Recently, evanescent wave cavity ring-down spectroscopy (EW-CRDS), has been developed as a fundamentally new measurement capability for characterization of interfaces and thin films. In contrast to conventional CRDS, which employs narrow-spectral-bandwidth mirrors and is applicable only to the gas-phase, EW-CRDS employs a miniature, monolithic, total-internal-reflection-(TIR)-ring cavity of regular polygonal geometry with at least one convex facet to induce stability. Evanescent waves generated by TIR probe absorption by matter in the vicinity of the cavity. Optical radiation enters and exits the resonator by photon tunneling, which permits precise control of input and output coupling. Furthermore, the broadband nature of TIR circumvents the narrow bandwidth restriction imposed by dielectric mirrors in conventional gas-phase cavity ring-down spectroscopy. The use of evanescent waves in spectroscopy is the basis for the well-established technique know as attenuated total reflectance (ATR). Yet conventional ATR lacks the sensitivity required to address many key problems in interfacial science and technology. EW-CRDS combines the advantages of cavity ring-down and ATR spectroscopies to achieve a synergistic new technology that exceeds existing optical absorption techniques in sensitivity by many orders of magnitude and may ultimately achieve single molecule detection.

Results and Future Plans: A theoretical model for the EW-CRDS TIR-ring cavity technology has been developed that incorporates all of the design variables related to cavity size, stability, and finesse, as well as the electrodynamic details of evanescent wave absorption and photon tunneling. The model permits optimum cavity designs to be identified. A square, TIR-ring cavity has been fabricated from ultra-high-purity fused silica. This cavity permits a wide variety of processes occurring in and on thin films to be studied in the near-UV to the near-IR. Since the chemical response of a surface is established over a much shorter length scale (≈1-5 nm) than the evanescent wave decay length, the surface response of a semi-infinite medium is obtained. Experiments on the adsorption of iodine by EW-CRDS have achieved a detection limit of <100 parts-per-million (ppm) of a monolayer. Reaction of I_2 to form I_3^- in the presence of adsorbed water can be observed and quantified. Furthermore, by measuring the ring-down time for the s- and p-polarization components separately, the average orientation of adsorbed molecules can be sensitively extracted.

EW-CRDS uniquely permits the sub-monolayer spectroscopy and chemistry of insulating surfaces to be probed. The SiO_2 surface itself, i.e., the intrinsic surface of the fused-silica minicavity, is very important in many industrial and environmental systems. Therefore, future investigations will likely include extension of EW-CRDS to the near infrared where the absorption bands arising from the surface silanol (SiOH) groups can be probed. The surface chemistry of SiO_2 is typically dominated by the reactions of the surface silanol groups, so exploring this spectral region will likely provide decisive insight. Since the transmission of high-purity SiO_2 in the mid-infrared is extremely high (≈1 dB/Km), EW-CRDS will likely achieve a detection limit of 1 ppm of a monolayer or better for SiOH. Furthermore, by using a continuous wave laser diode as the near-infrared source, a continuous wave implementation of EW-CRDS will be developed that will increase performance and range of application. Additional advances in the EW-CRDS technology are also expected that will extend the technique to liquids and to the mid-infrared spectral region through new cavity designs and different cavity materials.

Publications:

Pipino, A.C.R., ***"Evanescent Wave Cavity Ring-Down Spectroscopy for Ultra-Sensitive Chemical Detection,"*** Proc. SPIE Vol. 3535, International Symposium on Industrial and Environmental Monitors and Biosensors, Boston, Mass. November 1998.

Pipino, A.C.R., Hudgens, J.W., and Huie, R.E., ***"Evanescent Wave Cavity Ring-Down Spectroscopy as a Probe of Surface Processes,"*** Chem. Phys. Lett. 280, 104 (1997).

24. Property/Structure Relationships in Gelling Systems

H.J.M. Hanley, C.D. Muzny, and B.D. Butler

Objective: To measure *in-situ* the structure, properties, and dynamics of a gelling system, especially of a system gelling under the influence of an applied shear or stress; to develop scaling relationships to better understand the mechanism of gel formation; and to predict and, if possible, control the properties of the gel.

Problem: The sol-gel process is used to fabricate high-tech products at low process temperatures: materials with unique chemical compositions, porous glasses, ceramics of very high chemical purity, high-temperature superconductors, and materials with superior insulating properties are examples. The commercial success of the technology, however, requires that the product be manufactured to within a defined tolerance. This is often not achieved. The technical challenge is to understand the mechanism better and to devise a procedure to satisfy this goal. The specific challenge is to come up with an on-line, real-time procedure that can be used to optimize the sol-gel fabrication process and to control the properties of a final product. A novel challenge is to investigate whether materials might be produced using the sol-gel process via a continuous casting process. It is, therefore, important to understand the structural changes that take place in a shearing gel.

Approach: Our program is based on the premise that the properties and behavior of a system are a macroscopic reflection of how the structure responds when the system is perturbed. Hence, if the structure can be elucidated, the properties of the material can be predicted. The approach is to employ small angle neutron scattering (SANS) and laser light scattering as nondestructive probes that study the structure of the precursor sols and the subsequent gel at length scales ranging from about one nanometer to over a micron. The majority of the SANS experiments are performed on the spectrometers at the NIST Center for Neutron Research, Gaithersburg. Light scattering experiments are carried out in the NIST Boulder Laboratories. Studies of the systems under shear make use of a scattering cell incorporated in a constant stress rheometer that is placed in the neutron or light beam. The apparatus is capable of high accuracy measurements with viscosities that can range over about ten orders of magnitude. Dynamic information from gelling samples is extracted from the laser light experiments and measurements of the time for local structural rearrangement to take place in the gel, times on the order of a microsecond to a second. We have proposed a scaling rule to relate characteristics of the structure with the gelation time. We also carry out extensive computer simulations on models of gelling systems that help us better understand both our experimental data and the gelation process itself.

Results and Future Plans: Recently the viscometric properties and structure of dense sheared colloidal gels, formed at a pH of 8 from a commercial aqueous sol of 7 nm diameter silica particles, were investigated. We showed that, as the system gels under a constant shear rate, the viscosity at first increases, then peaks when the shear stress reaches a shear-rate-independent threshold value, and finally decreases asymptotically to approximately one tenth the peak value. We have indicated that this low viscosity state can apparently be held indefinitely by maintaining the shear but the system gels once the shear is removed. An abrupt change in the character of the SANS intensity was observed at the time corresponding to the peak in the viscosity. Given this information it was concluded that the drop in viscosity corresponds to a structural densification of growing clusters of the colloidal particles, and that this transformation occurs once the critical stress is reached. Future work will include studies of molecular gels, extension of our probes into the micron length region using an ultra-SANS spectrometer, investigations of the chemistry of the gelation process, and studies of a gelling system subjected to oscillatory motion.

Publications:

Butler, B.D., Muzny, C.D., and Hanley, H.J.M., ***"Scaling of Small-Angle Neutron Scattering Intensities from Gelling Colloidal Silica,"*** Int. J. Thermophys. (in press).

Hanley, H.J.M., Muzny, C.D., Butler, B.D., Straty, G.C., Bartlett, J., and Drabarek, E., ***"Shear Induced Restructuring of Dense Colloidal Silica Gels,"*** J. Physics: Condensed Matter (in press).

25. *Advanced Metrology to Determine the Structure and Dynamics of Disordered Systems*

H.J.M. Hanley, C.D. Muzny, G.C. Straty (Contractor), and B.D. Butler

Objective: To investigate the nanoscale architecture of complex disordered systems, to characterize a given system by defining its structure over distances ranging from about one nanometer to microns, and to develop the necessary metrology based on *in-situ* probes of the system using radiation scattering.

Problem: Disordered systems - for example; gels, precipitates in petroleum fluids, polymeric solutions and melts, micelles and macromolecules in solutions, inorganic/organic complexes - are part of modern technology. The problem is to be able to predict their properties and to control their behavior.

Approach: Our program is based on the premise that the properties and behavior of a system are macroscopic reflections of how the structure responds when the system is perturbed. Hence, if the structure can be elucidated, the properties of the material can in principle be predicted; likewise, if the structure can be altered, the behavior of the system can be controlled.

Results and Future Plans: The work has involved small angle neutron scattering (SANS) using spectrometers at the NIST Center for Neutron Research, Gaithersburg. Disordered phenomena investigated include surfactants and micelle formation, the sol-gel transition and the formation of inorganic/organic complexes and their surface structure. Many of the recent studies have made use of a constant stress rheometer adapted so that a Couette cell can be placed in the neutron beam. The apparatus is capable of high accuracy measurements with viscosities that can range over about ten orders of magnitude. Studies with this set-up include correlating the alignment of macromolecules with their viscosity in solution, and extensive investigations relating structure changes with viscometry of gelling colloidal silica.

Laser light scattering equipment has been developed at the NIST Boulder Laboratories to explore the structural changes in a system that take place at submicron and micron length scales. Further, we have adapted the light scattering equipment to extract dynamic information from a particular sample. Applications of the dynamic light scattering procedure include studies of the growth of nanoscale complexes and on-line, real time investigations of gelation.

Future plans include extending our investigations of gelling systems into the ultra-SANS region. More generally, we will introduce X-Ray scattering into our program to complement and extend the SANS and light scattering capabilities; if successful, NIST will then have the potential not only to investigate materials over the wide range of length scales, but also will have the flexibility to investigate systems with the most appropriate scattering tool. X-Rays are sometimes limited as a probe since they are absorbed strongly by most materials: hence, studies on systems that require a robust apparatus are often ruled out. Nevertheless, X-Rays give data with good resolution, require a small sample area, and offer the ability to change the scattering contrast of the high-Z elements.

By contrast, neutrons can identify the low-Z elements (including hydrogen) and have good penetration into a sample. They are thus particularly suited for studies of organic molecules in solution. Small angle neutron beams, however, are of relatively low flux, require large sample areas, and provide data with generally poor resolution. We intend, however, to work at the powerful Advanced Proton Source which is just now coming on-line at Argonne National Laboratory. In addition to employing high energy X-Rays for conventional static structure determinations, we intend to use these unique X-Ray beams for time correlation fluorescence spectroscopy. In this way it should be possible to investigate the microscopic dynamics in systems that are optically opaque.

Publications:

Straty, G.C., Muzny, C.D., Butler, B.D., Lin, M.Y., Slawecki, T., Glinka, C.J., and Hanley, H.J.M., ***"A Rheometric Shearing Apparatus at the NIST Center for Neutron Research,"*** Nucl. Instr. Meths. Phys. Res. A408, 511 (1998).

26. Molecular Dynamics Model of Retention Mechanisms

R.D. Mountain and J.T. Slusher

Objective: To develop a molecular model to examine mechanisms and molecular properties involved in Reversed-Phase Liquid Chromatography and to implement the model in a molecular dynamics simulation.

Problem: The investigation of retention mechanisms in reversed-phase liquid chromatography is a topic of current interest. This interest reflects the substantial difficulty in understanding the behavior (and thus our ability to predict/optimize) in these complex systems.

Approach: A molecular model of a pore in a chromatographic column has been developed. The pore is represented as a slit with long chain molecules attached to the surfaces of the slit. The solvent, water, methanol, acetonitrile, or mixtures of these substances, fills the space between the chain molecules. This model is simulated using existing molecular dynamics methods. Particular care is necessary to include the long-range electrostatic interactions between the solvent molecules. We use a form of the Ewald summation method applicable to this situation where translational symmetry is broken in one dimension.

The retention tendency for a system consisting of a solute, the solvent, and the chain type and packing density is examined by determining the change in the free energy of the system as the solute moves from the center of the slit toward the chain molecules. These are time consuming simulations that would be impossible to complete if conventional, serial simulation methods were used. Fortunately, this model lends itself to parallel processing with good scaling with up to eight to ten processors before the communication overhead reduces the efficiency of simulation.

Results and Future Plans: The model has been carefully tested for a methane solute in an acetonitrile/water mixture. The free energy of the system is lowest when the solute is in contact with the chain molecules. In this region of the slit, the solvent is mostly acetonitrile as the water is found primarily in the center of the slit. Although the flow rate in reality is typically much lower than can be considered in this type of simulation, the conclusion that methane would be "retained" is obvious since it would reside mainly in the lowest flow velocity part of the system.

The model will be applied in the future to more interesting solutes, initially benzene. The computational details of the model are being reviewed to see if computational efficiencies can be realized. In particular, an alternative formulation of the Ewald summation is being studied.

Publications:

Slusher, J.T. and Mountain, R.D., *"A Molecular Dynamics Study of a Reversed-Phase Liquid Chromatography Model,"* NIST Internal Report 6222 (1998).

Slusher, J.T. and Mountain, R.D., *"A Molecular Dynamics Study of a Reversed-Phase Liquid Chromatography Model,"* J. Phys. Chem. (submitted).

27. Advanced Methodology for Simulation of Fluids

B.D. Butler*, L. Lue, D.J. Evans (Aust. Nat. Univ.), L.V. Woodcock (Univ. of Bradford), and S. Gay (Univ. Colorado)*

Objective: To develop new methods for the advancement of the science of simulating fluid systems: to improve our ability to study single component and more complex multicomponent atomic and molecular models, both in and out of equilibrium; and to improve current predictive models of fluid properties through a better understanding of these idealized systems.

Problem: By providing an 'ideal' laboratory in which to study the behavior of a large number of interacting particles, computer simulation is an important tool in the study of the thermodynamics of fluid systems. Currently, computer simulation is not effective at predicting the behavior of actual fluids with an accuracy required, for example, by chemical engineers in the design of commercial separation processes. This is not only because current computational resources limit our ability to solve such complex problems - the particular methods and simulation algorithms used also need to be improved if progress is to be made in this area. Computer simulation is not just used to directly predict the behavior of real systems. In fact, it is often most effectively applied to lend insight into the fundamental nature of the structure and dynamics of complex systems. These insights, for example, have been incorporated into semi-empirical equations that are used by engineers for the prediction of fluid properties in technologically important systems. The improvement of computer modeling algorithms and methods are thus essential for progress to continue in the development of the prediction tools required by U.S. industry.

Approach: Our simulation activities concentrate on areas of current interest in the Division. The process of aggregation in quenched systems as models of gelation phenomena, the effects of shear on the thermodynamic states of fluids, steric effects in binary systems and their implications on solid-fluid equilibrium, and critical behavior in dilute polymer solutions are some examples of the simulation studies being done. By identifying and isolating weaknesses in current methods and theories, alternatives are developed, tested, and improved upon.

Results and Future Plans: Recent studies of quenched systems using Monte Carlo methods have helped lead to the concept of a 'configurational temperature' that was derived from fundamental thermodynamic principles and that allows one to compute the temperature of a simulation from knowledge of the particle positions and the potential through which they interact. This measure of the temperature has been used as a check for internal consistency in Monte Carlo programs and in molecular dynamics simulations of sheared systems to properly account for anomalous heat conduction effects. Aggregation phenomena have been investigated in systems with a modified potential function that contains a short-range attractive, but long-range repulsive component. Many interesting effects observed in real aggregating systems, such as network formation and the appearance of a 'hole' in the structure factor at small wave vectors, have been reproduced using this new potential. Methods to study depletion forces that arise from entropic considerations in binary hard-sphere systems have been also been developed. These Monte Carlo based methods helped to overcome the difficult problem of simulating systems that have two widely different relaxation rates. Monte Carlo methods were used to test a crossover theory for dilute polymer solutions and helped to elucidate the validity of the theory in certain regimes. Future plans include the incorporation of the concept of the configurational temperature to the thermostatting of nonequilibrium molecular dynamics (NEMD) models, studies of concentrated dendritic polymer solutions, the study of shear on aggregation processes, and tests of theoretical predictions of vapor-liquid, liquid-liquid, and liquid-solid phase equilibria in binary mixtures.

Publications:

Butler, B.D., Ayton, G., Jepps, O.G., and Evans, D.J., ***"Configurational Temperature: Verification of Monte Carlo Simulations,"*** J. Chem. Phys. 109, 6519 (1998).

28. *Molecular Theory of Solid-Fluid Equilibrium*

J.C. Rainwater, *D.G. Friend, P.D. Beale (Univ. Colorado), and S.G. Gay (Univ. Colorado)*

Objective: To develop a theory of solid-fluid equilibrium for pure systems and mixtures, including hydrocarbons, refrigerants, and other compounds of industrial interest.

Problem: The complete thermodynamic description of a pure fluid or fluid mixture requires knowledge of the fluid-solid boundary. For many processes it is important to know the location of, and to avoid, freezing conditions. Mixtures can have a variety of interesting solid-liquid phase diagrams, including miscible solids, single eutectics, and solid compounds with multiple eutectics. Also of interest are the crystal structure of the solid, the heat of fusion, and the volume change on freezing.

Approach: We start with the approach of P. A. Monson and co-workers of the University of Massachusetts. The solid is described by the cell model of Lennard-Jones and Devonshire, in which the free volume is calculated for a single molecule in a cage of fixed neighboring molecules within a specified lattice structure. As a modified approach, known as the fluctuating cell model, the positions of the cage molecules are allowed to fluctuate. The molecules are initially modeled as assemblies of hard spheres, and subsequently van der Waals attractive terms and quadrupole or dipole moments are added as perturbations. The liquid free energy is obtained from a simulation, and the phase boundary is determined by the double-tangent construction. This approach can be extended to more complex molecules with arbitrary geometries and multipolar interactions.

Results and Future Plans: We have completed a study of the methyl chloride system, in which the molecules are modeled as heteronuclear dumbbells with dipole moments. We found that the experimentally known crystal structure, more open than the initially expected close-packed structure, did not even have a solid-liquid transition in the absence of dipolar interactions, but the inclusion of dipole moments made a solid-liquid transition possible, and, in fact, favored the experimental structure over the close-packed structure. Use of the more open lattice also substantially improved predictions of the volume change on freezing and the ratio of triple-point to critical-point temperature. These results are comparable to those found by Monson and co-workers for a variety of homonuclear molecules with quadrupole moments. We are currently studying the problem of freezing into plastic crystals by means of extensions of the cell model. We have found, in two and three dimensions, an alternative to calculation of the free volume by Monte Carlo integration. We have solved analytically the integration over spatial coordinates, so that the remaining angular integrations can be performed efficiently by quadrature. For the two-dimensional homonuclear dumbbell system, we have implemented the fluctuating cell model with cage fluctuations determined from a single simulation, and the calculations are significantly more efficient with semianalytic integration. The less efficient alternative is to set up the lattice with springs on the molecules (the Einstein crystal) and to perform many simulations as a function of spring constant. We find that the fluctuating cell model agrees with simulation much better than the fixed cell model for molecules of moderately small bond length that form plastic crystals. We are at present developing code for semianalytic integration to extend the approach to three dimensions. Future work includes similar study of molecules of three and four atoms, and application to compounds such as other methyl halides, carbon monoxide, dimethyl ether, the butane isomers, and to simple mixtures.

Publications:

Gay, S.C., Beale, P.D., and Rainwater, J.C., "***Solid-Liquid Equilibrium of Dipolar Heteronuclear Hard Dumbbells in a Generalized van der Waals Theory: Application to Methyl Chloride,***" J. Chem. Phys. 109, 6820 (1998).

Gay, S.C., Beale, P.D., and Rainwater, J.C., "***Thermodynamic Perturbation Theory Applied to the Dipolar Heteronuclear Dumbbell Fluid,***" Molec. Physics (in press).

29. Primary Acoustic Thermometry

D. Ripple (Process Measurements Division), M.R. Moldover, and K.A. Gillis

Objectives: (1) To reduce the uncertainty in the determination of the thermodynamic temperature by a factor of 3 to 8 in the range from 500 K to 900 K using speed-of-sound measurements in low density argon as a primary standard, and (2) to improve the accuracy of the high-temperature fixed points (e.g., tin point, zinc point) and radiometry tied to these fixed points.

Problem: The most accurate determinations of thermodynamic temperature above 700 K use relative radiance measurements referenced to a black body near 700 K. The thermodynamic temperature of the black body is known from NIST constant volume gas thermometry (CVGT) experiments. Unfortunately, two NIST CVGT experiments differ from each other for reasons that are not well understood. The difference leads to an estimated uncertainty of 13 mK in temperatures near 700 K and 50 mK in temperatures near the gold point (1337.33 K).

Approach: We shall measure the frequencies of both acoustic and microwave resonances in a spherical, argon-filled cavity bounded by a thick, metal shell which in turn will be enclosed by a high-performance thermostat. The data will determine the speed of sound in the argon from which the thermodynamic temperature will be deduced. The temperature will be transferred to platinum resistance thermometers and then to fixed-point devices. For acoustic thermometry, the measured quantities are frequencies and the temperature. This contrasts with CVGT, which requires the measurement of pressures and temperature; thus, systematic effects will be very different in the present work and may resolve the discrepancies in the CVGT.

Results and Future Plans: Microwave and acoustic data in the temperature interval 217 K to 303 K had been acquired with a prototype resonator. These data were analyzed and a detailed manuscipt was prepared for publication. These data determined ($T - T_{90}$), the difference between the Kelvin thermodynamic temperature T and the International Temperature Scale of 1990 (ITS-90) with a standard uncertainty of 0.6 mK. The uncertainty depended mostly upon the model fitted to the acoustic data. The manuscript contains many specific suggestions for improving both the apparatus and the analysis. These suggestions are being implemented in the high-temperature apparatus.

A significant technical challenge was to develop electro-acoustic transducers that are compatible with the high temperatures and which neither contaminate the argon nor significantly perturb the resonance frequencies. During the past year, the resonator was reworked and transducers were installed. The pressure vessel and furnace were fabricated and assembled. Extensive portions of software were written to run the apparatus in a fully automated mode.

During the next year, the resonator will be installed in the furnace. Both acoustic and microwave resonances will be measured, first at ambient temperature and then at higher temperatures. The flowing-gas concept will be tested and optimized. The acoustic transducers will be characterized at high temperatures.

Publications:

Moldover, M.R., Boyes, S.J., Meyer, C.W., and Goodwin, A.R.H. ***"Thermodynamic Temperatures of the Triple Points of Mercury and Gallium and in the Interval 217 K to 303 K,"*** J. Res. NIST (in press).

30. *Advanced Refrigeration Systems for Cryogenic Applications*

R. Radebaugh*, P. Bradley, E. Marquardt, M. Lewis, J.H. Xiao (Chinese Academy of Sciences), J. Braun (Purdue Univ.), M. Hill (Univ. Colorado), and J. Gary and A. O'Gallagher (Applied and Computational Mathematics Division, ITL)*

Objective: To develop new refrigeration techniques and improved refrigerator components for the temperature range of 120 K and below and to investigate and use measurement and modeling techniques for evaluating performance of cryocoolers and their components, such as heat exchangers.

Problem: Cryocoolers are required for many technology areas, including the cooling of infrared sensors for surveillance and atmospheric studies, the cooling of superconducting electronics and magnets, the cooling of cryopumps for clean vacuums in semiconductor fabrication processes, the liquefaction of natural gas for clean-burning transportation fuel, and many other existing and potential applications. The use of these technologies has been hampered because of problems with existing cryocoolers. These problems include short lifetimes, inefficiency, high cost, and excessive vibration. Improved cryocoolers would stimulate the growth of all these technology areas.

Approach: Precision moving parts in existing cryocoolers are a source of wear, vibration, and high cost. Our approach in the development of improved refrigeration processes has been to focus our measurements and modeling on processes that eliminate most or all moving parts while still maintaining high efficiency. Much of our research has been on pulse tube refrigerators, which have no cold moving parts, and on the ThermoAcoustically Driven Orifice Pulse Tube Refrigerator (TADOPTR), which has no moving parts in the entire system and is a joint invention of NIST and Los Alamos National Laboratory. Our studies encompass measurements and modeling of losses to further improve efficiencies of these cryocoolers while increasing their lifetimes and simplifying construction techniques. NIST research in this area has much industry and other government agency support to aid in the transfer of this technology to industry.

Results and Future Plans: During FY98, measurements were made on the thermal conductance of packed lead spheres, which are commonly used in regenerative cryocoolers for use in cryopumps. From measurements at various helium filling pressures, we have determined that most of the heat is transported by the helium gas a distance of about 4 μm across the boundary rather than by the direct metallic contact. The thermal conductance degradation factor was found to be 0.11. Almost no prior data existed for the thermal conductances of these packed materials, but they are needed for the optimum design of regenerative heat exchangers in many types of cryocoolers, including pulse tube refrigerators and Gifford-McMahon refrigerators. Measurement techniques are now being developed where thermal conductance in regenerators can be measured *in-situ*.

Under a CRADA with Lockheed Martin of Denver we have optimized and measured the performance of the world's smallest pulse tube refrigerator designed for flight on the Space Shuttle. The system was incorporated into the Shuttle in January 1998 and launched in April 1998. Upon return it was determined that the batteries used to provide the power failed due to the vibration of the launch. Tests of the pulse tube refrigerator and all electronic controls after the launch showed they worked exactly as they did before launch. Improved batteries have been procured and the system is ready for a second Space Shuttle flight as promised by NASA, although a date has not been set.

Publications:

Lewis, M.A., Kuriyama, T., Kuriyama, F., and Radebaugh, R., ***"Measurement of Heat Conduction Through Stacked Screens,"*** Adv. Cryo. Eng. 43, 1611 (1998).

31. Microscale Heat Transfer

R. Radebaugh, E. Marquardt, M. Lewis, J. Seigwarth, J.H. Xiao (Chinese Academy of Sciences), and M. Hill (Univ. Colorado)

Objectives: To develop models and correlations for predicting heat flow between fluids and solids in cases where the length or time dimensions are very small and to carry out experimental measurements to improve the modeling and correlation efforts.

Problem: The miniaturization of many devices such as electronics, medical probes, laser diodes, cryocoolers, etc., is hampered by the difficulty in removing heat from very small dimensions or during very short times. In most cases the heat must be transferred from a solid to some fluid. Often the fluid serves to carry the heat to another location where the heat can be dissipated over a larger region to the environment. Our knowledge of the mechanisms for heat transfer in very small dimensions is limited, and, as a result, it is difficult to properly design a device for adequate heat transfer that will not lead to overheating. In the case of oscillating heat transfer, such as in many types of cryocoolers, the system size can be miniaturized by utilizing high frequency oscillations. Difficulties in transferring heat in very short time scales limit the operating frequency and, hence, the size reduction that can be achieved.

Approach: The early stages of this program involve a review of the literature on microscale heat transfer to determine prior efforts and to find where there are the largest gaps in our ability to predict heat transfer in very small length or time scales. The scale sizes of importance to our study are in the region where the more conventional bulk or steady state heat transfer calculations and correlations can no longer be used with any accuracy. In the case of short time scales we are extending our prior work on regenerative cryocoolers to investigate the effect of frequency on heat transfer and pressure drop in regenerators where helium gas is the working fluid. A normalized frequency parameter, known as the dynamic Reynolds number or the Valensi number, will be used to study correlations of heat transfer and pressure drop with frequency. Existing models will be studied to verify their applicability for these cryocooler applications. In the case of heat transfer in small length scales, we are most interested in understanding the limitations to increased heat transfer density. The systems to be studied include single phase and two phase heat transfer to allow a comparison between the two mechanisms. Multicomponent fluids are also to be studied because of their ability to be in two phases over a wide temperature range, thereby enhancing heat transfer in a heat exchanger that spans a wide temperature range.

Results and Future Plans: In 1998 we studied the effect of small time scales at the lowest temperatures that can be reached with regenerative cryocoolers. Theoretical models were developed to explain why high frequency operation (f >10 Hz) of regenerative cryocoolers at temperatures below about 20 K require low porosity regenerators to maintain high efficiency. Details of the model need to be developed further to generate design guidelines for this region of operation. High frequency operation in this temperature range is of considerable interest in a wide variety of applications because of the possibility of achieving high efficiency and compact size. We have also designed an experimental apparatus to measure microscale heat transfer coefficients and friction factors with flowing single-phase and two-phase fluids. We have developed new fabrication techniques to manufacture large numbers of microscale perforated plate heat transfer test specimens. Plans for 1999 include the construction of the experimental apparatus and measurement of single-phase heat transfer in very small dimensions. The influence of high velocities, such as jet impingement, on heat transfer and friction factors will be considered in the experiments. Comparisons with heat and mass transfer in macroscale geometries will be made.

Publications:

Xiao, J.H. and Radebaugh, R., ***"Effect of Frequency on the Performance of Low Temperature Regenerative Refrigeration,"*** Cryocoolers 10 (in press).

32. NATO Advanced Study Institute on Molecular Energetics

K.K. Irikura

Objective: To exchange technology in the area of molecular energetics with NATO members and associated countries.

Problem: Chemical thermodynamics and kinetics data are increasingly important industrially, both in the traditional chemical manufacturing industry and in newer areas, such as microelectronics, that rely heavily upon novel chemistry. New computational and experimental techniques are constantly being developed to supply needed data, and it is difficult for scientists to remain knowledgeable.

Approach: Assemble an international team of scientific experts to teach a NATO ASI course (see http://www.nato.int/science/) entitled *Energetics of Stable Molecules and Reactive Intermediates*. The Director was M.E. Minas da Piedade (Instituto Superior Técnico, Lisbon, Portugal) and the other members of the organizing committee were K.K. Irikura (NIST), M. Tilset (Univ. Oslo, Norway), and J.A. Martinho Simões (Univ. Lisbon, Portugal).

Results and Future Plans: 90 scientists attended, representing 17 nations. Scientifically, NIST had the dominant presence. Three of the 18 lecturers were from NIST (Div. 838). There were two organized discussions of the strengths, weaknesses, and future of thermochemical databases, with heavy emphasis on the NIST Chemistry WebBook. NIST scientists (K.K. Irikura and R.D. Johnson III) also organized and conducted a laboratory course that featured commercial software for computational chemistry and also selected NIST databases, including the WebBook. This course was attended by about 60 scientists, triple the expectations. Some trends emerged from the conference. (1) Experimentalists are relying increasingly upon quantum chemistry to support, corroborate, or even replace experimental measurements. (2) Electronic, on-line databases are very important. (3) Critical evaluation of literature data is very important but much more difficult than is usually appreciated.

The school achieved its goals and will result in a book published by Kluwer and edited by Prof. Minas da Piedade. The materials for the laboratory course in computational thermochemistry will be revised and published by NIST on the world-wide web.

Publications:

Irikura, K.K. ***"Extracting Thermochemical Information from ab initio Data,"*** in Energetics of Stable Molecules and Reactive Intermediates; M.E. Minas da Piedade, Ed.; Kluwer: Dordrecht, 1999.

VI. Analytical Chemistry Division (839)

Willie E. May, Chief

A. Division Overview

Mission:
The Analytical Chemistry Division serves as the Nation's reference laboratory for chemical measurements and standards to enhance U.S. industry's productivity and competitiveness, assure equity in trade, and provide quality assurance for chemical measurements used for assessing and improving public health, safety, and the environment. The Division's activities primarily contribute to the accomplishment of CSTL's measurement science and measurement standards goals through the efforts of its five Groups:

- Spectrochemical Methods
- Organic Analytical Methods
- Gas Metrology and Classical Methods
- Chemical Sensing and Automation Technology
- Nuclear Analytical Methods

Programs:
Research in the Division is focused on the phenomena that underpin the measurement of chemical species in a broad spectrum of matrices. The skills and knowledge derived from laboratory-based research are applied to the development and critical evaluation of measurement methods of known accuracy, precision, sensitivity, and selectivity. This expertise in chemical measurement science is deployed in a highly leveraged manner and serves as the foundation for cross-cutting measurements and standards programs in:

- Advanced Materials Characterization
- Analytical Instrument Performance and Calibration
- Environmental Monitoring and Technology
- Forensics
- Healthcare and Food/Nutrition

Our vision is to maximize this leverage by establishing and maintaining the infrastructure for providing national traceability and assessing international comparability of chemical measurements for these and future high priority program areas with infrastructural tools such as:

- Standard Reference Materials
- NIST Traceable Reference Materials (NTRMs)
- measurement quality assurance programs in critical national areas, and
- comparisons of NIST primary methods and standards with other national metrology laboratories.

Increased requirements for quality systems documentation for trade and effective decision-making regarding the health and safety of the U.S. population have increased the need for demonstrating "traceability-to-NIST" and establishing a more formal means for documenting measurement comparability with standards laboratories of other nations and/or regions. Standard Reference Materials (SRMs) are certified reference materials (CRMs) issued under the National Institute of Standards and Technology trademark that are well-characterized using state-of-the-art measurement methods and/or technologies for chemical composition and/or physical properties. Traditionally, SRMs have been the primary tools that NIST provides to the user community for achieving chemical measurement quality assurance and traceability to national standards. Currently, NIST catalogs nearly 1300 different types of SRMs; in 1998 NIST sold nearly 37,000 SRM units to approximately 6,650 unique customers. Approximately 21,000 of the units sold were from the 850 different types of materials that are certified for chemical composition. Since it has the world's leading, most mature, and most comprehensive reference materials program, most of the world looks to NIST as the de facto source for high quality CRMs to support chemical measurements.

NIST has met the reference materials needs of U.S. industry and commerce for nearly 100 years. While our reference materials program has focused primarily on U.S. requirements, it is clear that these materials address international measurement needs as well. As demonstration of quality and "traceability" for chemical measurements have become increasingly global issues, the need for internationally recognized and accepted CRMs have increased correspondingly. Their use is now often mandated in measurement/quality protocols for analytical testing laboratories. Coupled with the fast pace of technological change and greater measurement needs, the demand for additional quantities and additional specific varieties of reference materials has mushroomed. NIST, by itself, does not have the resources to provide SRMs (exact sample types, unique compound combinations, concentrations, etc.) to meet all these needs. Without a significant shift in paradigm, we will not to be able to address future needs for reference materials; either nationally or internationally.

The NIST Traceable Reference Materials (NTRM) program was created to address the problem of increasing needs for reference materials with a well-defined linkage to national standards. An NTRM is a commercially produced reference material with a well-defined traceability linkage to existing NIST standards for chemical measurements. This traceability linkage is established via criteria and protocols defined by NIST and tailored to meet the needs of the metrological community to be served. The NTRM concept was implemented initially in the gas standards area to allow NIST to respond to increasing demands for high quality reference materials needed to implement the "Emissions Trading" provisions of the Clean Air Act of 1990 (while facing the reality of constant human and financial resources at NIST). The program has been highly successful. Since its inception, ten specialty gas companies have worked with NIST to certify nearly 5600 NTRM cylinders of gas mixtures that have been used to produce approximately 400,000 NIST-traceable gas standards for end-users. According to Stephen Miller, Technical Director, Scott Specialty Gases, "the NTRM program has served as an excellent vehicle for production of the high quality standards – of known pedigree – required by both industry and the regulatory community in the implementation of Title IV [SO2 emissions trading] of the 1990 Clean Air Act." The NTRM model for the commercial production of reference materials is being extended to other mature and high volume areas to both more effectively deliver the increasing number of NIST-traceable standards to end users and allow more of our internal resources to be diverted to address new and/or more difficult measurement problems. Immediate plans are to provide NTRMs for optical filter standards, elemental solution standards, and metal alloy standards.

In addition to our efforts to define and establish a national infrastructure for supporting comparability of chemical measurements, we are aggressively expanding our efforts to document the comparability of NIST primary methods and standards with those of other nations and metrological regions. We engage in both multilateral (BIPM Consultative Committee on the Amount of Substance) and strategic bi- and trilateral collaborations. Our bilateral program with the NMi (The National Metrology Institution of the Netherlands, which also represents the European Union, for determining the equivalence of primary gas standards has resulted in a formal "Declaration of Equivalence." The U.S. EPA and European environmental regulatory bodies mutually recognize this "Declaration" as documenting the equivalence of seven NIST and NMi primary gas mixtures suites (spanning a wide range of concentrations). Collaborations for assessing the equivalence of primary standards are planned with DFM (Denmark) and OHM (Hungary) for solution conductivity, with PTB (Germany) for pH, with NIMC (Japan) and BAM (Germany) for elemental solution standards, and with NIMC for volatile organic compound standards.

Other federal and state government agencies continue to be important customers. During the past year, we were involved in 13 projects with six federal and state government agencies primarily providing them with measurement quality assurance services for environmental and health-related activities. As part of a government-private sector partnership, we have begun to work with the EPA, States, and other public and commercial entities to establish appropriate oversight of a new effort to externalize and improve the Nation's environmental laboratory chemical measurement proficiency testing programs (PT). Since the 1970s, EPA has conducted semiannual PT studies to assess the competence of over 6,000 public and private sector laboratories to conduct analyses required by the Clean Water and the Safe Drinking Water Acts. At the end of this year, the cost-free provision of these services will be phased out and replaced by a multi-provider system in which interested states and private companies will provide these PT services on a fee-basis. We continued our work with NOAA and the EPA to provide measurement quality assurance (interlaboratory comparisons and SRM development) for approximately 40 laboratories involved with the measurement of organic contaminants in marine sediments and tissues as part of various marine-monitoring programs. Our interactions with the National Institute of Justice focus on developing measurement methods and standards for the analysis of drugs-of-abuse in hair, developing and applying cutting-edge statistical approaches for the analysis and visualization of DNA profiling data for laboratory performance evaluation, and developing and methods and standards for the forensic analysis of gunshot and explosive residues were also continued. Compliance with the Chemical Weapons Convention is a critical international issue. We are working with the Defense Special Weapons Agency and the Organization for the Prohibition of Chemical Weapons to develop and critically evaluate chemical measurement protocols to be used during onsite inspections of manufacturing and storage facilities. We completed our interactions with eight laboratories that were involved in the measurement of heavy metals, pesticides, and PAHs in soil, water, food, and indoor/outdoor air samples collected and analyzed as part of the EPA National Human Exposure Assessment Study. Though funding from the National Cancer Institute ended last year, we are continuing our quality assurance program for approximately 60 laboratories world wide involved in the measurement of fat soluble vitamins, carotenoids, and ascorbic acid in human serum. This is part of studies to determine the cancer preventive benefits of dietary intakes of selected micronutrients to high risk human populations. This program, which had been supported for past 15 years by the NCI, will be maintained, although at a reduced level of activity, due to the strong need expressed by the participating laboratories. It will be supported through a combination of fees from the participating laboratories and reprogrammed Division resources. A new measurement quality assurance-related activity was initiated during the past year with the Department of Energy Radiological and Environmental Science Laboratory in Idaho Falls designed to establish NIST-traceability for all organic and inorganic contaminant measurements being made by DoE contractor laboratories at and around DoE waste sites throughout the U.S.

Selected Programs Highlights:

Details concerning these and additional interactions and collaborations with other government agencies can be found in the brief group overviews and selected Technical Activity Reports that follow. These overviews and reports illustrate the synergistic relationships among the research activities in chemical measurement science based in the various groups and the standards and quality assurance activities underway in the various program areas.

Spectrochemical Methods

Research activities in spectrochemical methods are directed toward the development, critical evaluation, and application of techniques for the identification and measurement of inorganic species using X-Ray, optical, and mass spectrometries. The focus of this research is measurement accuracy and precision, benchmarking industry's needs for traceability, advanced materials characterization, and commodity value assignment and specification.

The Group made a major investment in state-of-the-art analytical instrumentation in the past year, with the procurement and installation of two inductively coupled plasma mass spectrometers (ICP-MS), a glow discharge optical emission spectrometer (GD-OES), and an X-Ray fluorescence spectrometer (XRF) and an associated fusion sample preparation machine. These instruments will provide a strong basis for our research and measurement programs well into the next century and will complement the advanced laboratory facilities that will soon house them.

The refurbishment of the XRF laboratory continues the Group's commitment to this technique and is an expansion of its use in our standards program. We immediately applied the new spectrometer to several projects, the most important being the renewal of three cement SRMs. The cement industry is a significant component of the U.S. economy with annual shipments valued at $4.2 billion. The dispersed nature of the industry, coupled with vast quantities used in commerce, results in extremely large numbers of cement analyses made by analytical service laboratories. The construction industry depends on NIST cement SRMs to maintain its laboratories' qualifications for ASTM Standard Methods for cement, and XRF is the principal method used for these analyses. Certification measurements were made using a single critically evaluated NIST method, and interlaboratory measurements are provided by the industry using a industry standard method – an ASTM Standard Method for cement in this case. NIST certification measurements were made using calibrations from custom-made standards prepared by fusion of high purity compounds. This approach represents the ultimate in type standardization since the primary standards and unknowns are both in the same form (glass) and concentrations of the elements span very narrow ranges. In the coming year, seven additional cement SRMs are scheduled for renewal.

Last year we described an important research development that significantly improved the performance of ICP-Optical Emission Spectrometry (OES) with advanced methods of signal treatment. As predicted last year, we have applied the technique in several prominent Division measurement programs and, at the same time, are more broadly exploring the research opportunities it affords. During the past year, ICP-OES employing this new signal treatment approach was used in the certification of over 20 spectrometric solution SRMs. For the single element solutions, the median relative standard error of replication was 0.033 % and of calibration was 0.042 %, resulting in a median Type A relative uncertainty of 0.053 %. See Technical Activities Report 3 for further details.

The improved ICP-OES method has been presented in the context of "replacing classical analysis." It matches the precision and approaches the understanding of sources of error of classical analysis, especially for cases where the sample can be reduced to a simple dilute solution, as is the case for the spectrometric solution SRMs. This year we have pushed the technique a bit farther and determined the major elements (Ni, Mo, Cr, and Co) in a high temperature alloy. A multi-element experimental plan and calibration strategy was applied and the results will allow certification of these elements with the very narrow uncertainty limits needed by industry, but heretofore only attainable with wet chemical methods. Because of the rigor and labor intensity required, classical analysis is an expensive and disappearing capability in analytical chemistry. Thus, there is great interest by laboratories in being able to procure this capability from analytical instrument manufacturers. We will continue to explore intelligent and robust applications of these advanced methods and promote the process of technology transfer both by working with manufacturers and by demonstrating and publicizing our results. The initial article published this year in **Analytical Chemistry** will be the first of many detailing and promoting this research.

The Group made significant forward strides in its glow discharge optical emission program. We purchased a new spectrometer and established a CRADA with the LECO Corp., the only U.S. manufacturer of GD-OES instrumentation, to broadly investigate this technique's capabilities for quantitative determination of non-metallic elements in solids. This year, a GD-OES method for the determination of C, P, S, and Si in grey cast iron was developed and critically evaluated through analysis of a series of three grey cast iron CRMs. Results showed good agreement with certified values, with the mean relative bias across the three unknowns and four analytes being 1.4 %. From the perspective of U.S. industry, the ability to determine these elements quantitatively using GD-OES relieves the need to maintain multiple analytical methods, providing significant economic benefit. Details concerning this activity are provided in Technical Activities Report 20.

Inductively coupled plasma mass spectrometry (ICP-MS) is now the measurement workhorse for the Group, continuing the trend begun in 1985 when the first instrument was procured. This year, we procured two new instruments, one being a high-resolution instrument with significantly enhanced capabilities, and we shut down the first instrument after 13 years of successful operation. In 1985, the broadly stated sensitivity level was a million counts per second per µg/mL in solution; the new instruments approach 100 million counts per second per µg/mL in solution. This high sensitivity and broad elemental coverage are the two factors that make ICP-MS so versatile and valuable.

This year, we explored two areas to improve the accuracy of ICP-MS measurements: the use of electrothermal vaporization (ETV) to eliminate oxygen interference and methods to correct and control instrumental mass bias. The ETV sample introduction method made possible isotope ratio measurements, and sulfur was determined in coke and fuel oil by ID-ICP-MS with comparable results to ID-TIMS (thermal ionization mass spectrometry) on the same samples. Mass bias has traditionally been corrected by bracketing sample measurements with isotopic standards. In this procedure over 40 % of the sample load consists of the measurement of isotopic standards. We have investigated an alternative approach that allows mass bias correction to be performed at the same time the analytical isotope ratio is measured. This "internal" correction procedure involves the measurement of three isotopes, using one isotope pair to correct the second isotope pair by assuming a functional relationship between mass bias and mass difference. This procedure appears to be considerably more efficient, and equally accurate. Details concerning these two projects funded through our Division Reserve Program are provided in Technical Activities Reports 1 and 2, respectively.

The full range of optical, X-Ray, and mass spectrometric techniques available in the group were applied in the past year to the certification of inorganic constituents in reference material matrices: metals, fuels, dust, blood, and paint films, among others. These reference materials are the principal means of transferring NIST measurement accuracy to the nation's inorganic chemical measurement community and are the basis of its chemical measurement infrastructure.

Organic Analytical Methods:
Research activities in organic analytical methods are directed toward the development, critical evaluation, and application of methods for the identification and measurement of organic and organometal species using organic mass spectrometry and analytical separations techniques. These include gas chromatography (GC), liquid chromatography (LC), supercritical fluid chromatography (SFC) and extraction (SFE), capillary electrophoresis (CE), and capillary electrochromatography (CEC).

Recent research activities in organic mass spectrometry have focused on the development of techniques for characterization and quantitative determination of proteins in biological matrices. We are establishing reference methods for important biomarkers such as troponin-I (a new marker of myocardial infarction), glycohemoglobin (an important new marker for diabetes), and serum thyroxine (an important marker for thyroid function). Techniques have been developed for the chemical characterization of purified troponin-I preparations, thus providing a means for comparing structure with results from field studies involving immunoassays. An isotope dilution GC/MS method for cortisol (a marker for endocrine function) has been developed and is undergoing testing. Development of accurate methods is an important component of our ongoing collaborations with the **College of American Pathologists** and **the Centers for Disease Control and Prevention** to establish NIST traceability for measurement of important health markers. A new LC/MS instrument is providing us with new capabilities for the determination of analytes of health, nutritional, forensic, and environmental importance, as well as for structural studies of natural products. Our new high-resolution mass spectrometer provides the high precision measurements needed for our clinical standards program. It is now being applied to the development of capabilities for measurement of environmental contaminants such as dioxins, furans, and toxaphene, which will lead to certification measurements of these substances in environmental matrix SRMs.

Recent research activities in separation science have focused on investigations of the physical and chemical processes that influence the separation and detection of organic compounds, and the application of these techniques in the development of reference methods for the determination of these compounds in natural matrices. The results of these investigations are used to design stationary phases tailored to solve specific separations and analysis problems. Our recent efforts have focused on application of CEC to clinical and environmental separation problems. The combined use of CEC with C_{30} stationary phases, developed in this laboratory, has resulted in greatly improved separations of ß-carotene isomers and other carotenoids of interest in health and food/nutritional studies. Remaining challenges include the incorporation of gradient elution capability with CEC. Equipment has been developed to utilize LC in combination with CEC. This hybrid instrumentation will permit more reliable operation and will facilitate gradient elution separations of analytes with widely divergent properties. We have recently used the technology developed for making CEC columns in the development of a novel precolumn affinity-capillary electrophoresis (PA-CE) method for the on-line enrichment and measurement of troponin I in serum. The PA-CE approach, which utilizes silica immobilized antibodies to selectively enrich the troponin I from the serum, has wide applicability to the measurement of other disease marker proteins. We are currently working to expand this approach to include on-line digestion and structural analysis of proteins or nucleic acids using silica immobilized enzymes. Our current research in chiral separations focuses on the development of CE and SFC separation strategies for optical isomers of pharmaceutical and agricultural interest. Recent work demonstrated the applicability of pectins, which are common constituents of many fruits and vegetables that are used as food additives, to enantiomer separations in CE. We also developed strategies for the combined achiral/chiral separation of components of drug formulations by SFC. This approach may help to eliminate the need for separate achiral and chiral analytical methodology.

We have developed a method using pressurized fluid extraction and gas chromatography/mass spectrometry to assess the micro-homogeneity of organic contaminants in natural environmental matrices. Sample size is at the 1 mg to 100 mg level. The method has been applied to air particulate, diesel particulate, and sediment SRMs (see Technical Activity Report No. 4).

Our research in organometal speciation has continued with improvements in the gas chromatography-atomic emission detection method for the determination of methylmercury and alkyl tin species. The new method, which includes a derivatization step and a solid phase micro-extraction (SPME) step to concentrate the analytes, will be used to provide certification measurements for several SRMs including fish tissue, mussel tissue, oyster tissue, and blood.

A number of new SRMs are being developed to support measurement activities in the environmental, health-care, and food/nutritional communities. Over 70 analytes including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated pesticides, and trace elements have been certified (and another 80 analytes as reference values) in a new sediment material, New York/New Jersey Waterway Sediment (SRM 1944). SRM 1944 will be the first NIST natural matrix SRM with values assigned for the concentration of polychlorinated dibenzo-*p*-dioxins and dibenzofurans; these results were obtained as part of a 14 laboratory comparison exercise coordinated by NIST and Environment Canada. Several environmental matrix SRMs that had been issued previously were reanalyzed to provide a much larger number of constituents with certified or reference values. These SRMs include Urban Dust (SRM 1649a), Diesel Particulate Matter (SRM 1650a), Organics in Cod Liver Oil (SRM 1588a), and PCBs in River Sediment (SRM 1939a). For example, SRM 1649 was first issued in 1981 with certified and reference values for 14 PAHs. Whereas the reissue, SRM 1649a, has certified/reference values for 80 PAHs, PCBs, and chlorinated pesticides as well as values for total organic carbon, percent extractable material, carbon composition, particle size information, and trace elements. The replacement material for PCBs in Human Serum (SRM 1589a) has been prepared with the PCBs at naturally occurring levels in contrast to the original material in which high levels of PCB Aroclor mixtures were added to the serum. SRM 1589a has been analyzed at NIST and the Centers for Disease Control and Prevention to provide certified and reference values for PCBs, pesticides, and polychlorinated dibenzo-*p*-dioxins and dibenzofurans. Material has been collected and processed for a new "fillet of fish" SRM that will be certified for PCBs and chlorinated pesticides, and will also be characterized for proximate content (proteins, carbohydrates, fat, etc.) to serve the needs of the food/nutritional as well as the environmental measurement communities.

SRM 2890, Water Saturated *n*-Octanol, was recently issued for the calibration of Karl Fischer instrumentation for the determination of trace levels of moisture in liquids (see Technical Activity Report No. 5). We have also prepared several of the 26 primary standard solution SRMs (SRMs 3061 through 3086) required in support of the EPA Proficiency Testing program for their water analysis programs. Certification measurements have been completed for a Meat Homogenate (SRM 1546), identified by the USDA, FDA, and the food industry as a high priority need. The canned meat homogenate has certified values for cholesterol, six fatty acids, calcium, sodium, iron, and total nitrogen, and reference values for proximates (total fat, carbohydrate, protein, water, and ash), calories, a number of other fatty acids, and some additional nutrients (see Technical Activity Report No. 12). As a result of a recommendation from a recent NIST workshop involving the food industry, FDA, and USDA, we provided additional information on constituents of nutritional interest, e.g., proximates and fatty acids, in 10 existing food matrix SRMs and RMs. SRM 1546 and these other recently updated food-matrix reference materials will be used by the food testing/nutritional laboratory community to facilitate compliance with nutritional labeling laws and to provide accurate labeling information to assist consumers in making sound nutritional choices.

In the clinical area, measurements have been completed for renewal of Bovine Serum Albumin (SRM

927c) an important standard for total protein assays. Renewal measurements are underway for Fat-Soluble Vitamins, Carotenoids, and Cholesterol in Human Serum (SRM 968c), a widely used standard in the clinical community for evaluating the accuracy of methods used to determine vitamins in serum as part of nutrition and chemoprevention studies. A new frozen serum SRM for the determination of ascorbic acid (SRM 970) has been recently certified. Work has been completed for two pure organic SRMs, Sucrose (SRM 17e) a standard for optical rotation measurements and sugar purity assays, and Cystine (SRM 143d) a standard for elemental analyses of C, H, N, and S.

Gas Metrology and Classical Methods:
Research activities within this group are focused on gas metrology, classical wet chemical methods (gravimetry, titrimetry), coulometry, ion chromatography, optical spectroscopy, and maintenance of the theoretical infrastructure for pH and conductivity measurements.

In collaboration with EPA and the remote sensing community, we are developing the quantitative database of infrared spectra required for establishing FTIR-based technology as a reliable tool for real-time monitoring for airborne chemical contaminants along plant boundaries and within plant facilities. Because the spectra are being prepared using NIST primary gas standards, well-defined traceability to NIST can be established for any subsequent field measurements. These spectra will be required to be used in the new update of EPA method TO-16. More information concerning this activity, and the recent release of a CD-ROM containing spectra for the 21 highest priority species, can be found in Technical Activities Report 14.

In U.S. industry and throughout the private sector pH is the most used, and in many instances the most critical, chemical test. Within the Classical Methods team we maintain the national standards for pH and participate in international forums to define the pH scale. Over the past two years we have been defending the traditional pH scale from being replaced with a simpler, less technically defensible scale supported by many in the academic field. Since pH measurements are integral to many manufacturing processes and medical procedures, this shift to an alternate scale would have had a major economic impact. This past year, with considerable help from other National Metrology Laboratories, we were successful in maintaining the traditional pH scale for high accuracy measurements. More information on our pH program and the international debate can be found in Technical Activity Report 24.

During FY98 the following SRMs were completed; 17 gas cylinder, 21 spectrometric solution, two conductivity, five ion activity, two Zeolite, and six Volatile Organic Compound solutions. A total of 192 gas cylinder SRMs were recertified for 14 companies. While these standards are critically needed, their continuous production ties up considerable fiscal and human resources and limits our ability to address new standards needs. The NIST Traceable Reference Materials (NTRM) Program was created to address this concern. In FY98, we worked with eight specialty gas vendors to certify 71 NTRM batches. The 1400 individual gas cylinders in these certified batches will be used to produce approximately 100,000 NIST-traceable gas standards for end-users.

Over the next year we will be searching for international collaborators to certify gas cylinder SRMs. The intent is to "second source" gas cylinder SRMs so that this critical resource will be available at all times to our worldwide customer base. There are many issues to resolve for this concept to operate effectively. Further discussion regarding this topic can be found in Technical Activity Report 25.

To assist the U.S. automobile industry, we are developing and evaluating new analytical measurement tools and providing standards needed to address compliance issues associated with the Clean Air Act of 1990. We are developing an infrared-based sensing device and are working with the NIST Physics Laboratory to evaluate a new Fourier Transform microwave device for real-time detection of oxygenated hydrocarbons in automobile exhaust. A series of new cylinder-based gas SRMs for low emission vehicles also are being produced to support U.S. automobile manufacturers in the development of the next generation of "clean" cars. For example, we are currently developing low concentration (<5 μmol/mol) nitric oxide gas standards to meet future regulations on automobile emissions. This effort will take approximately two years to complete and will result in new gas cylinder SRMs, since these standards are not suitable for the NTRM program. We will be collaborating with NMi and NPL in this effort to assure that low NO standards are comparable around the world. Additional details concerning this activity can be found in Technical Activity Report 7.

Chemical Sensing and Automation Technology: The Chemical Sensing and Automation Technology Group is being renamed the Molecular Spectrometry and Microfluidic Methods Group (MS&MM) to reflect better its activities and responsibilities. The MS&MM Group conducts research on the metrology of molecular spectrometry and develops standards for calibration, validation, and performance of instruments for measuring molecular spectra; conducts research on microfluidic devices, methods, and applications for chemical analysis including studies of materials and material properties affecting the flow of liquids in microchannels and the use of microchannel and other electrophoretic methods for forensic and toxicological applications and standards; has responsibility for the development and certification of optical transmittance and wavelength standards in the ultraviolet, visible, and near-infrared spectral regions; and works with users and manufacturers of analytical instruments to assess and measure the performance of analytical methods and to determine and address existing and future needs for analytical instrument standards ranging from device calibration and instrument performance through specifications for remote device control and data interchange.

In FY98, 124 solid absorbance filter SRMs were certified, and 203 optical filter sets were recertified. In addition, 500 units of SRM 931f (Liquid Absorbance Standard for Ultraviolet and Visible Spectrophotometry) and 250 units of SRM 2034 (Holmium Oxide Solution Wavelength Standard from 240 nm to 650 nm) were certified with assistance from two Guest Researchers from CENAM. In the course of certifying 98 units of the new near infrared wavelength standard (SRM 2035), we developed a fractional center-of-gravity peak picking algorithm that provides acceptable wavelength precision on peaks of varying shapes without overly compromising the human perception of the peak location. We hope that this will be the basis of a NIST-wide wavelength picking algorithm.

A significant effort is underway to complete the second high accuracy reference ultraviolet-visible spectrophotometer. Consultants have been contracted to develop the instrument control software and we have begun the process of testing the instrument's components and verifying and validating the system performance.

The new project to develop Raman intensity standards was initiated. Over 66 glasses, many of them custom made for this purpose, have been examined as potential standards. We assembled a stable light source featuring an integrating-sphere-illuminated optical fiber and had it calibrated in the Optical Technology Division of PL. This known intensity source, traceable to the cryogenic radiometer, is used to provide absolute calibration of the Raman instruments being used to develop the intensity standard. The new dispersive Raman instrument came on line. It is being validated and calibrated.

The optical filters NTRM program gained momentum in FY98 with the successful completion of two workshops. Drafts of documentation describing the detailed operation of the filters NTRM program have been completed. It appears that initially there will be four to six companies as NTRM producers.

Our microfluidics efforts have been augmented with a five-year competence project funded by the NIST Director for our Microscale Analytical Laboratory proposal. This activity is a joint effort with the Process Measurements Division. It will focus on:

- developing new analytical concepts, new chemistries, and detection methods for microchannel devices,
- understanding the properties of plastics relevant to their use in microchannel devices,
- creating new system design and fabrication techniques for microchannel devices, and
- developing a standard test bed to evaluate parameters important to the behavior of microchannel devices.

In FY98 three summer students were involved in microfluid-related projects and several important collaborations were developed with faculty at regional universities.

Four synthetic "reformulated" gasoline SRMs (2294 through 2297), which compliment several other oxygenate in reference fuel SRMs, were certified for total sulfur. Oxygenate content, and benzene information values were provided for the hydrocarbon constituents. Our novel near infrared analysis technique was used to check the quality of the ethanol-reformulated fuel SRM by directly analyzing the liquid in the sealed vials.

Working with Guest Researchers from the Fochhochschule in Wiesbaden Germany, we have extended the Consortium on Automated Analytical Laboratory Systems (CAALS) device capability dataset (DCD) concept to the system level. In addition to containing all of the DCDs for the system's components, the system capability dataset (SCD) includes information about inter-device dependencies and interactions, system error detection and handling, and shared resources. Christian Piotrowski and Thorsten Richter received first and second prizes for their posters on the DCD and SCD concepts at the **Lab Automation 98** conference in San Diego.

Nuclear Analytical Methods:

Research activities in this Group are focused on the science that supports the identification and quantitation of chemical species by nuclear analytical techniques. Current laboratory research activities involve the full suite of nuclear analytical techniques including instrumental and radiochemical neutron activation analysis (NAA), prompt gamma activation analysis (PGAA), and neutron depth profiling (NDP), as well as applications of neutron focusing technology for analytical applications. The measurement capabilities that reside within this group provide an excellent complement to those in the Spectrochemical Methods Group in that they depend upon characteristics of the nucleus of the element rather than the electron shells, and also that they often are nondestructive and do not require sample dissolution.

NAA is a powerful reference technique that has been used at NIST for many years. New developments continue to provide improvements in detection sensitivities, elemental specificity, precision, and overall accuracy that allow it to address new measurement needs. We have recently been developing INAA procedures and applying them to study the homogeneity of SRMs at small sample sizes. Many analytical techniques used in industry and academia rely on the analysis of very small samples (i.e., 1 mg), typically in the solid (undissolved) form. Unfortunately most SRMs are certified with minimum sample sizes of 100 mg - 500 mg, and are therefore unsuitable for use as control materials for these techniques unless additional information is made available. Taking advantage of the sensitivity and nondestructive properties of INAA, the use of this technique for homogeneity studies of small samples has been evaluated and implemented for the determination of sampling characteristics for a number of biological SRMs and air particulate matter. The minimal analytical uncertainty associated with the INAA measurements allows extraction of the variability due to material inhomogeneity from the observed total variability in a set of measurements.

This year we have investigated three sediment materials that have shown the potential for a high degree of homogeneity at very small sample sizes for possible use as a future SRM aimed at solid-sampling analytical techniques. One deep ocean sediment (Pacific Ocean "Site M") showed good to excellent homogeneity (at sample sizes below 1 mg) for seven trace and minor elements; studies of additional elements are in progress. Another candidate material may be the fine fraction of SRM 1944; cooperation with the Organic Analytical Methods would be indicated. Evaluation of the Ingamells model describing homogeneity has been initiated with the Statistical Engineering Division.

This year, we have developed and critically evaluated a radiochemical method to determine phosphorus in metals using beta counting. A method to accurately determine P at low levels is needed since the concentration of this element affects the properties of many advanced materials. Other, non-nuclear, analytical techniques face severe problems, including blank levels and interferences, when attempting to determine P at the µg/g level. RNAA is essentially blank free, and the ability to add mg levels of stable P after sample irradiation permits the isolation of this element from all other radioactive nuclides. Such isolation is important since spectrometric techniques cannot be used to quantify beta emitters. However, the ability to track the beta emission as a function of time and compare this to the known half life of ^{32}P provides an extremely valuable quality assurance check.

Pioneering research is conducted within this Group on the use of cold neutron beams as analytical probes for both PGAA and NDP. PGAA measures the total amount of an analyte present throughout a sample by the analysis of the prompt gamma-rays emitted immediately following neutron capture. NDP on the other hand, determines the concentrations of several important elements (isotopes) as a function of depth within the first few micrometers of the surface by energy analysis of the prompt charged particles emitted during neutron bombardment. Both of these techniques continue to make important contributions in the characterization of advanced materials, particularly with the enhanced sensitivities now available using the cold neutrons from the NIST Reactor.

We have been studying the error sources that affect cold-neutron PGAA to a different extent than they affect thermal-neutron PGAA for the last several years. This is particularly important for neutron scattering and neutron self-shielding effects. Ratio techniques, including k_0 approaches can greatly minimize such errors. We are continuing to make high-accuracy measurements of detector efficiency and element ratios (with respect to titanium) in order to determine more accurately the k_0 factors for cold neutron PGAA, thus improving the accuracy of the method and providing a check of traditional approaches.

We have begun routine application of high resolution NDP boron measurements using Li recoil particles. A paper has been published summarizing initial work. Several problems have been identified including elevated background from energy overlay and low energy tail. Some problems with the published data for stopping power for the Li ion in different materials have also been identified. Progress has been made in terms of automating the energy to depth conversion using a PC program. The current measurements made on a boron in silicon multlayer, demonstrated 10 % - 15 % improvement using Li recoil particles.

The cold neutron PGAA and NDP spectrometers, which are available to outside researchers as part of the NIST Center for Neutron Research national users facility, continue to provide high-quality measurements for outside scientists. Current experiments of interest at the NDP instrument include:

- the measurement of nitrogen profiles in thin TiN films in conjunction with Intel Corp.,
- lithium migration in electrochromic films in cooperation with SAGE Electrochromics and Penn State University, and
- the characterization of boron and nitrogen thin films in a wide variety of materials for high tech applications.

Non-destructive, matrix-independent measurements of hydrogen by the cold neutron PGAA technique have become particularly valuable in view of the difficulties of accurate determination of this element by other techniques. In fact, most of the current PGAA experiments involve measuring hydrogen in a host of materials for applications involving:

- metal embrittlement studies,
- materials studies for development of new types of lithium batteries,
- materials studies for development of new types of fuel cells, and
- providing H concentrations for materials prior to neutron scattering measurements.

Other measurements made this year at the PGAA facility include:

- determination of Cr/V ratios in magnetic alloys of potential use for the information storage industry,
- characterization of antiferromagnetic compounds that are of interest to the superconductor industry,
- boron in mineral separates to develop light element standards for use in geochemical analyses,
- determination of chromium in a chromite layer deposited on steel casings that are used in Kraft recovery boilers in the pulp and paper industry, in order to recover the chemicals used to dissolve the lignin binding the fibers in wood, and
- measurement of the neutron capture cross section and capture spectrum of ^{208}Pb. The capture cross section of this doubly magic nuclide is important for understanding the s-process nucleosynthesis of the lead and bismuth isotopes in stars. Published information on this cross section is sparse and imprecise.

Efforts continue within the Group to develop the techniques and methodology of focusing cold neutron beams for analytical applications of PGAA and NDP. A monolithic lens consisting of a fused tapered bundle of polycapillaries that provides a smaller focus of about 0.15 mm (FWHM at the focal spot) has been installed in the NDP chamber. The chamber has also been modified to accept a separate lid through which the lens can be mounted for remote-controlled alignment. A new alignment system containing a CCD camera with vacuum capability has also been installed. It provides a spatial resolution of 12 μm (pixel size) and an 8 bit dynamic range for the neutron intensity, and a possibility for charged particle imaging. Together with the new vacuum-compatible motion stages, the alignment system permits Video Radiation Detection (VRD) measurements without breaking the vacuum. Further, the lens can be retracted out of the beam for measurements on the same sample with normal NDP geometry. The new lens and focusing system now give us the capability of measuring samples as small as ≈0.1 mm in diameter or, together with our current scanning system, of measuring concentrations in three dimensions with much improved spatial resolution. Previously, our three dimensional profiles were performed with beam spot sizes of 1 cm.

Future Directions

All Division research and service projects are reviewed on an annual basis for quality, progress, and match to mission and customer needs. The chemical measurement science and crosscutting program areas on which the Division's research and measurement service activities are focused will not change very much in the coming year. However, we will continue to redirect some of our efforts from chemical sensing and automation technology to expand our programs in analytical instrument calibration transfer and performance and clinical biomarker standards. As mentioned earlier, we are also beginning a major new effort in microanalytical devices and measurement technology.

We will continue to focus more of the Division's resources on chemical measurement science and the development SRMs with improved accuracy and uncertainty levels, and establishment of the infrastructure for commercial production of NIST-traceable secondary standards to meet day-to-day end-user needs. The Division's budget for Standard Reference Materials activities has been ≈$3M for each of the past several years. During this period, the majority of our efforts have focused on renewals urgently requested by customers. As a result few resources have remained for development of standards to address new measurement problems/needs. The gas NTRM program described previously has provided some relief and over the past two years, we have been able to initiate efforts for development of a number of new, high priority SRMs including the following that should be completed during the coming year:

- Antibiotics in Milk (for QA of tests used to accept/reject more than 50,000 lots of milk per yr.),
- Fish Tissue (PCBs, pesticides, methylmercury and food proximates to be certified),
- Zeolite Catalysts (Na, Si, Al, Fe, and trace metals to be certified),
- Aircraft Alloys (P and S to be certified; materials failure related to P and S concentrations),
- Transmission NIR Wavelength Standard (for precise calibration of spectral region of increasing industrial interest),
- Moisture in Crude Oil (moisture levels, like sulfur, greatly influence the price of crude oils),
- Toxic Metals in Blood (toxic metals such as Cd, Pb, total and methylmercury to be certified), and
- VOCs in Methanol (provide accuracy benchmark and measurement traceability for PE tests provided to more than 5000 environmental testing laboratories by commercial vendors).

Work will begin on the following SRMs requested by the petroleum, clinical, food, and chemical process industries respectively:

- Lubricating Oil Additives (to certify 12 elements for providing QA and required measurement traceability for $5B/yr Lubricants Industry),
- Cardiac Troponin-I (new definitive biomarker of heart attack not being used extensively due to measurement problems),
- Baking Chocolate (to complement the suite of SRMs developed in response to nutritional labeling laws), and
- Reflective NIR Wavelength Standard (for precise calibration of spectral region of increasing industrial interest).

Approximately 20 SRM renewals will be completed this year and efforts will begin for re-certification of an additional 25 or so high priority materials. For the longer term future, we plan to re-institute the NIST program in luminescence standards. The highest priority will be the development of primary reference instrumentation to qualify SRMs for fluoresence.

We expect that the NTRM approach will continue to expand as the basis for allowing the commercial sector to provide reference materials to end-users with a well-defined traceability linkage to NIST. High quality SRMs will continue to be developed to address both national and international measurement problems, but they will be much more expensive and targeted for purchase primarily by other national metrology institutes and commercial producers/distributors. Increasingly, end-user needs will be met via NIST-traceable, commercially produced reference materials.

The complex nature of chemical measurements coupled with the increasingly global nature of trade, health, and environmental issues speaks to the need for having the world make measurements using a common "meterstick." The comprehensive nature of the NIST program in chemical measurements puts us in position to make a very significant contribution to the international chemical measurements community in this regard. In order to do this in both a cost-effective and internationally congenial manner, we are investigating opportunities for partnering with other highly qualified NMIs to provide high quality Certified Reference Materials in the following general categories.

- High Purity Neat Chemicals
- Organic Calibration Solutions
- Inorganic Calibration Solutions
- Gas Mixture Standards
- Optical Filter Standards
- Conductivity Standards
- Ion Activity Standards

Complex Matrix Standards

- Advanced Materials
- Biological Fluids/Tissues
- Foods/Botanical Materials
- Geological Materials
- Metal Alloys
- Petroleum/Fossil Fuels
- Sediments/Soils/Particulates

NMIs will be approached for partnership in a manner to assure representation from major international trading blocks. However, selection of partners in each standards area would be based primarily on benchmarking studies to determine/identify those most technically competent in each area. We will most likely use the gas mixture standards area as a testbed for this approach. Potential members would be NIST, NMi (the Netherlands), and NPL (UK) initially, with NIMC (Japan) to join in the future. Potential advantages of these proposed NIST/NMI partnerships include increased supply, breadth, and quality of reference materials for the worldwide chemical measurements community as well as less duplication of effort for more efficient use of limited resources.

Increased effort will be directed toward establishment of the chemical metrology infrastructure needed to facilitate trade and effective health and environmental monitoring and decision-making throughout the Americas. We will continue to participate and provide leadership in CCQM working groups in order to define Key Comparisons for assessing worldwide comparability of chemical measurement capabilities and standards. We will also continue to work through NORAMET and the Interamerican Metrology System (SIM) to plan and conduct comparisons in key chemical measurement areas and serve as a "gateway laboratory" to connect non-CCQM member countries to the international chemical measurement community. We will also develop and offer formal courses at NIST concerning the use of advanced chemical measurement methods for certification of reference materials. The first series of courses; in organic analytical methods and spectrochemical methods are planned for the first week of December 1998 and courses in gas metrology, classical analytical methods, and nuclear analytical methods will follow in 1999.

The information that has been provided represents a broad range of research and service activities within the general area of chemical measurement science. This overview plus the Selected Technical Activity Reports that follow provide additional details concerning our work and reflect the high quality of our staff. This information also shows how our efforts are impacting U.S. industry's productivity and competitiveness as well as providing measurement infrastructural support for environmental quality and human health assessments

B. Selected Technical Reports

1. Reduction of O_2 Interference on the ICP-MS Determination of Sulfur Using Electrothermal Vaporization for Sample Introduction

L.L. Yu, W.R. Kelly, and R.D. Vocke

Objective: To reduce the amount of oxygen present in the plasma of an Inductively Coupled Plasma Mass Spectrometer (ICP-MS), thus reducing interferences caused by oxygen, and allowing the development of an isotope dilution ICPMS method for the determination of sub-µg/g sulfur.

Problem: The presence of oxygen in an ICP results in the formation of a variety of molecular ions that interfere with the determination of elements of the same mass. The problem is particularly severe for the determination of sulfur, where the molecular ions $^{16}O_2^+$, $^{16}O_2{}^1H^+$, and $^{16}O^{18}O^+$ cause large isobaric interferences at sulfur masses 32, 33, and 34. This has prevented measurement of this important element using ICPMS, the most convenient and prevalent variety of mass spectrometry for elemental analysis. The deleterious effects of sulfur as a pollutant and as a contaminant that affects the properties of many advanced materials make the sulfur measurements made at NIST among the most significant of NIST chemical measurements.

Approach: The normal means of introducing a sample into an ICPMS is to inject a water aerosol containing the sample into the plasma. The water that reaches the plasma in this process is the major source of oxygen in the ICP. An alternative sample introduction system under development is the electrothermal vaporizer (ETV). In this system the sample is again introduced as a water solution, but here a small volume of the solution is deposited in a small graphite furnace connected to the input of the ICP. The furnace is first gently heated to boil off the water, then raised to a high temperature, and the gases containing the contents of the sample residue are then injected into the ICP.

Results and Future Plans: The ETV was found to be effective at reducing the magnitude of the oxygen molecular ion interference at the sulfur masses, but some residual oxygen interference remained. Studies were undertaken that identified three secondary sources of ICP oxygen: the sample matrix, impurities in the plasma gas, and the leakage around the sampler cone that separates the high temperature atmospheric pressure ICP from the mass spectrometer. We found that the addition of N_2 to the ICP, which normally uses only Ar gas, had the effect of scavenging oxygen species in plasma, thus further reducing the interferences.

By using the combination of the ETV with the Ar-N_2 mixed gas plasma, the oxygen interferences were reduced to the point where isotope ratio measurements of sulfur in coke and fuel oil samples could be made. The ICPMS values determined in this manner were within 0.5 % to 1 % of the accepted thermal ionization (TIMS) values for these samples, which is within counting statistics for these measurements. The detection limit for the isotope dilution ETV sulfur method using masses 32 and 34 is estimated to be about 80 pg, or 4 ng/g for the typical 20 µL sample volume.

In the future, we will study the efficacy of using this method for the measurement of sulfur in high purity irons and high performance alloys. We plan to further investigate the mechanism of the nitrogen-oxygen interaction in the plasma. The techniques for the reduction of the oxygen background can be extended to the measurement of other elements suffering from oxide interferences.

2. *Characterization of Mass Bias in IC-PMS*

K.E. Murphy, L.L. Yu, G.C. Turk, S.E. Long, and E.S. Beary

Objective: To investigate the behavior of mass bias in inductively couple plasma mass spectrometry (ICP-MS), and examine different approaches to mass bias correction.

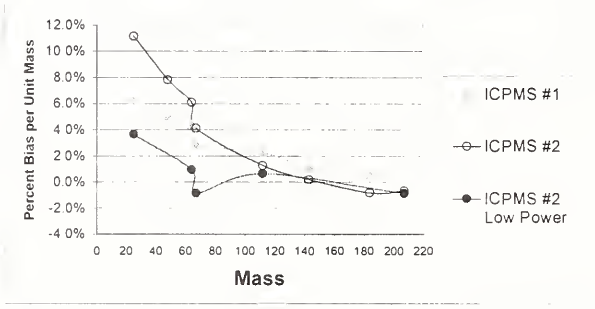
Problem: Isotope dilution ICP-MS is used extensively at NIST to provide accurate and precise measurements of elemental concentrations. Mass dependent variations in ion focusing and detection cause measured isotope ratios to be somewhat skewed from the actual ratios, and consequently, "mass bias" corrections need to be applied in an isotope dilution experiment. This mass bias is several percent for some elements and can drift throughout an analysis. Isotopic standards must be run repeatedly to determine the magnitude of the mass bias. A better understanding of the behavior of mass bias under different analytical conditions, and exploration of ways to correct for it, will result in improved measurement capabilities.

Approach: We have conducted experiments to compare the magnitude and stability of mass bias on different ICP instruments, with different instrument designs. Solutions were prepared containing a mixture of elements spanning the mass range. These test solutions were designed so that each element had at least three isotopes of similar abundance, allowing investigation of mass bias over large mass ranges (between elements) as well as across short mass ranges (between isotopes). The effect of sample matrix was also studied by adding a high concentration of a matrix element to the solution mixture.

The standard procedure for mass bias correction uses the measurement of an isotopic standard before and after every two samples, and assumes a linear drift with time. In this procedure over 40 % of the sample load consists of the measurement of isotopic standards. We have investigated an alternative approach that allows mass bias correction to be performed at the same time the analytical isotope ratio is measured. This "internal" correction procedure involves the measurement of three isotopes, using one isotope pair to correct the second isotope pair by assuming a functional relationship between mass bias and mass difference.

Results and Future Plans: Figure 1 shows typical mass bias vs. mass functions collected using the multielement mixtures on two different ICP mass spectrometers, and at different ICP power levels. The mass bias is expressed as a percent bias between the measured and true isotope ratios per unit mass difference. The magnitude of the mass bias is clearly different between the different instruments, and is affected by the RF power level and other factors. However, the general shape of the curve is quite consistent, showing decreasing mass bias with increasing mass. The anomalous shift that occurs between Zn and Cu was not expected, and is as yet not understood. Measurement of mass bias factors in matrix-laden solutions (containing 1000 mg/kg and 3000 mg/kg U) showed differences from 0.2 % to 2.0 % from mass bias factors measured in pure solutions. This is an important observation since mass bias corrections are generally made using matrix-free isotopic standards, yielding potentially biased results.

Fig 1. Mass Bias as a Function of Instrument and Plasma Power



The application of the three-isotope internal correction procedure in matrix-free samples yielded results comparable to traditional methods, but with a more efficient use of measurement time. Future experiments, involving the same comparison in matrix-laden samples may yet demonstrate further advantages of internal correction procedures.

3. *Moving ICP-OES Toward Primary Method Status*

M. Salit and G.C. Turk

Objective: To apply experiment design principles to permit inductively coupled plasma-optical emission spectroscopy (ICP-OES) to be considered as a primary method for determination of major component elements present in a sample.

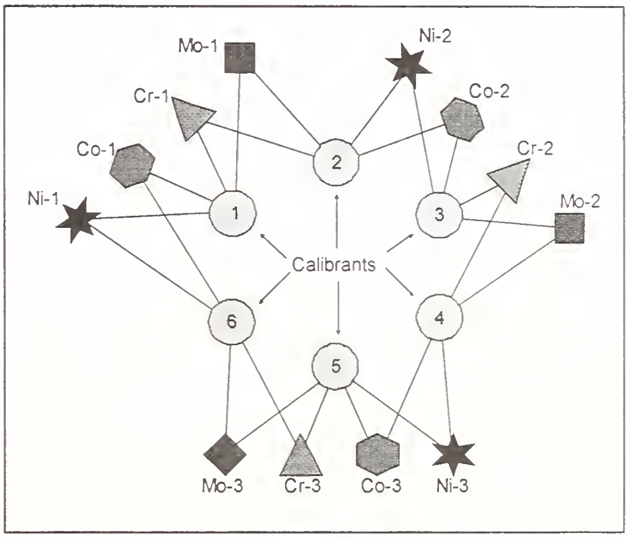
Problem: Recent research has led to an enhancement of ICP-OES measurement precision, and now offers an opportunity to supplant classical methods (titrations and gravimetric analysis) as a primary method for determination of the major constituents of a sample. A requirement for a primary method is that a complete uncertainty statement can be written in terms of SI units. With precision of signal measurement on the order of parts-per-ten-thousand, effects that were masked by noise are now significant components of uncertainty. These effects - potential bias from inter-element interferences and the variability of solution handling - must be captured to write a complete uncertainty statement.

Approach: A robust experimental design was developed for the ICP-OES analysis of a Ni-based high temperature alloy, in that the four elements (Ni, Cr, Co, and Mo) which together comprise over 98 % of the mass of the alloy would be determined. This design includes features not normally considered in an ICP-OES analysis, and serves as a test case for its consideration as a primary method.

The use of an internal standard is an important aspect of the measurement, permitting a robust ratio measurement, and rejecting the plethora of noise sources that effect the numerator and denominator in the same fashion. In this measurement, a "spike" from a different element is added quantitatively to the sample. A calibration relating measured signal ratio to mass fraction of analyte is established using a series of standards (calibrants) whose mass fraction ratio of analyte to internal standard is well known.

Uncertainty components due to measurement of samples and calibrants are readily assessed with replicate measurement. Uncertainty arising from sample-to-sample compositional variability and solution-to-solution preparation variability is captured with replicate sampling and preparation. Uncertainty associated with calibration arises from variability of the mass fraction ratio in the calibrants due to primary material purity, primary solution preparation, and calibrant preparation (dilution/addition of internal standard).

Pictured here is a multi-element calibration strategy which permits the different sources of variability to be identified and measured, with a crossed nature that allows errors to be logically deduced and bias from inter-element interference to be detected. All possible matrix compositions are spanned by the six unique calibrants, which are made up approximately in proportion from the elements that together comprise > 98 % of the matrix. Inter-element interference can be detected by the observation of anomalous calibration relationships amongst the different calibrants.



Results and Future Plans: Results consistent with classical and other spectroscopic methods were obtained, with smaller uncertainties. Further validation of this method of testing for bias will be pursued experimentally, with intentional perturbation with known interferences.

Publications:

Salit, M.L. and Turk, G.C. ***"A Drift Correction Procedure,"*** Anal. Chem. 70, 3184-3190 (1998)

4. *Chemical Microhomogeneity of Natural Matrix Environmental SRMs for Organic Components*

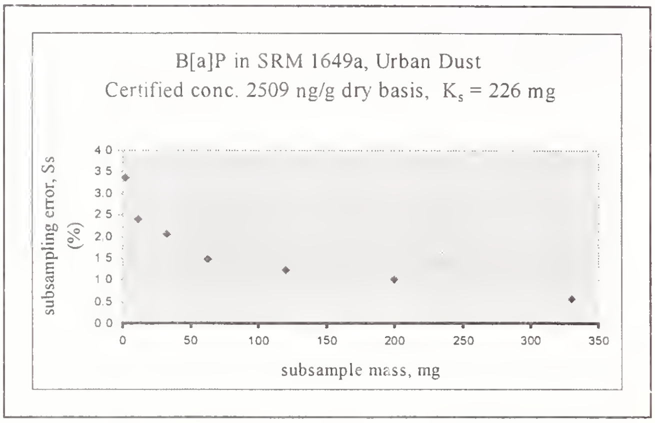
M.M. Schantz, M. Vangel (Statistical Engineering Division, ITL), and S.A. Wise

Objective: To develop methods for assessing the microhomogeneity of natural matrix SRMs for polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCB) congeners, and chlorinated pesticides.

Problem: During the certification of an SRM, particularly natural matrix materials, substantial effort is directed to the determination of the homogeneity of the material with respect to a given sample size and a specific analyte. The minimum sample size below which analyte homogeneity has not been assessed is stated in the Certificate of Analysis. For natural matrix SRMs certified for organic constituents (e.g., air particulate, marine sediment, mussel tissue, diesel particulate), we have generally extracted 1 g to 10 g subsamples for analysis using conventional Soxhlet extraction. The increasing sensitivity of techniques used for organic analysis has led to a need for methods to assess homogeneity of SRM subsamples of smaller size.

Approach: Recently, we have evaluated a pressurized fluid extraction (PFE) technique for the extraction of PAHs, PCB congeners, and chlorinated pesticides from a variety of SRMs. PFE is amenable to the extraction of samples as small as several milligrams. PFE with gas chromatography with mass spectrometric detection (GC/MS) has been used to probe the microhomogeneity of three natural matrix environmental SRMs: SRM 1649a (Urban Dust/Organics), SRM 1650a (Diesel Particulate Matter), and SRM 1944 (New York/New Jersey Waterway Sediment). For SRM 1649a and SRM 1650a, the PAHs have been quantified in samples of sizes from 1 mg to 400 mg and from 5 mg to 100 mg, respectively. For SRM 1944, in addition to the PAHs we have quantified PCB congeners and chlorinated pesticides in samples ranging in size from 10 mg to 700 mg.

Results and Future Plans: The Ingamells sampling constant (K_s) has been used as the first approximation to the homogeneity of these materials.



K_s is defined as the sample size of which the uncertainty due to sample heterogeneity is 1 %. An example of the plot of subsampling error versus the mass of sample extracted is shown for one PAH, benzo[a]pyrene (B[a]P). Results from using this approach showed that the sampling constant varies with the PAH concentration from 50 mg to 450 mg in the Urban Dust SRM but only from 40 mg to 75 mg in the Diesel Particulate Matter SRM.

We are currently working with the NIST Statistical Engineering Division to develop a model using these data to present micro-homogeneity information on NIST SRM Certificates of Analysis.

Publications:

Schantz, M.M., Nichols, J.J., and Wise, S. A., *"Evaluation of Pressurized Fluid Extraction for the Extraction of Environmental Matrix Reference Materials,"* Anal. Chem., 69, 4210-4219 (1997).

Reference:

Ingamells, C.O., *"New Approaches to Geochemical Analysis and Sampling,"* Talanta, 21, 141-155 (1974).

5. *Resolution of the Difference between Coulometric and Amperometric Karl Fischer Measurements of Water in Oil*

S.A. Margolis

Objective: To investigate sources of variation and bias in the measurement of water in oils by coulometric vs. amperometric Karl Fischer methods as a function of composition of a variety of hydrocarbons and hydrocarbon mixtures.

Problem: The measurement of trace levels of water in oils impacts a large number of industrial groups including the electric power industry, light and heavy industry, the military, and the oil industry. Accurate water measurements are essential in monitoring suitability of oils required for the efficient operation of the machinery. Different Karl Fischer methods often yield different concentrations of water in a given oil. Understanding the basis of this difference is essential for evaluating the accuracy of the various Karl Fischer methods.

Approach: Karl Fischer titration is the method of choice for the measurement of trace levels of water in oils (< 100 mg/kg). Most commercial testing laboratories use coulometric-based instrumentation for this titration, but the amperometric-based technique is also used. In previous studies we identified the lack of dissolutionin the reagent of oils prior to analysis as being an important source of bias. Greater understanding of this observation was obtained by measuring the water in a variety of hydrocarbons from hexane to hydraulic fluids. Saturated, partially saturated, and supersaturated oils were examined using both coulometric and amperometric Karl Fischer methods.

Results and Future Plans: The determination of water in hydrocarbons and hydrocarbon mixtures is a function of the types of hydrocarbons present in the material being analyzed. All Karl Fischer methods tested yielded comparable results for the amount of water in compounds such as xylene and octanol. For all oil samples, amperometric titrations of homogeneous solutions gave higher results than did coulometric titrations. Under heterogeneous conditions (two phases present in the titration cell), the amount of water measured amperometrically was 30 % - 50 % lower, similar to that found coulometrically. The two phases making up this heterogeneous mixture were separated and titrated amperometrically in a homogeneous system. All of the water not measured in the two-phase system was found in the oil phase, thus demonstrating that under heterogeneous conditions, some of the water is sequestered in the oil phase and unavailable for measurement.

During the past year SRM 2890, Water Saturated *1*-Octanol was certified for water (39.24 mg/kg ± 0.85 mg/kg) as a standard for the calibration of Karl Fischer instruments and other instruments used for the measurement of water in oils, foods, and fine chemicals. Future studies will include preparation of water in crude oil reference materials, comparison of the measurement of water in oils by Karl Fisher methods and FTIR, and the evaluation of other methods of moisture measurement that are used commercially such as oven evaporation and azeotropic distillation.

Publications:

Margolis, S., ***"Effect of Hydrocarbon Composition on the Measurement of Water in Oils by Coulometric and Volumetric Karl Fischer Methods,"*** Anal. Chem., 70, 4264-4270 (1998)

Margolis, S.A., "***Systematic Errors in Measurement of Moisture by Karl Fischer Methods,***" in: Proc. of the 3rd International Symposium on Humidity and Moisture, United Kingdom, 2, pp. 133-140 (1998)

6. *Development of Primary Standards for Ambient Global Warming Gases*

*G.C. **Rhoderick** and W.D. Dorko*

Objective: To develop ambient level gas standards of methane (CH_4), nitrous oxide (N_2O), dichlorodifluoromethane (CFC-12), and trichlorofluoromethane (CFC-11) to support the measurement of these species by the atmospheric research community.

Problem: Trace gases in the atmosphere have been suspected of being associated with changes in the earth's climate and some have been monitored for 40 years. The longest continual record of monitoring a trace species is for carbon dioxide (CO_2) for which monitoring began in 1958. CO_2 was chosen for study because it acts as a strong greenhouse gas and its concentration in the atmosphere was believed to affect the earth's temperature. Other trace species such as N_2O and CH_4 have also been identified as greenhouse gases. Still other species such as CFC-12 and CFC-11 have been identified as species that rise into the stratosphere and are active in destroying the earth's protective ozone layer. The atmospheric concentrations of these gases are monitored since they are regulated as part of the Montreal Protocol, an international agreement signed by the U.S., which attempts to limit the production and use of CFCs. The monitoring is used to determine compliance with the terms of the treaty.

Because there is no common source of accepted national gas standards for these species, the researchers making measurements of these gases in the atmosphere rely on their own standards or others to determine the concentrations. This can create a potential problem when trying to relate measurements from many sources due to lack of demonstrated comparability of the standards used. NIST SRM gaseous mixtures of these species would provide an accuracy basis and traceability for these measurements.

Approach: Development of NIST primary standards to support these measurements involved the preparation of three levels of concentrations of these species. The final third level consisted of eight primary gas standards containing CH_4, N_2O, CFC-11, and CFC-12 in an air matrix with the concentrations of each species bracketing the nominal atmospheric concentrations (CH_4 = 1.7 µmol/mol; N_2O = 312 nmol/mol; CFC-12 = 530 pmol/mol; CFC-11 = 270 pmol/mol). The pure starting materials were analyzed by gas chromatography (GC) using several different detectors and mass spectrometry to determine impurities, and the matrix air was analyzed for trace amounts of the compounds in question. The completed set of standards was then analyzed using GC to check for internal consistency.

Results and Future Plans: Data for the methane and N_2O resulted in very good linear calibration curves. The results show that the atmospheric level standards are in good agreement with no outliers. The agreement between standards is within an average of 0.1 % relative for CH_4 and 0.2 % for N_2O. Final uncertainties are expected to be in the 0.2 % to 0.4 % region. There appears to be a potential bias among the standards for CFC-11 and for CFC-12. More studies will be undertaken to resolve these discrepancies. Currently, standards from NOAA in Boulder, Colorado are being compared with the NIST set for CH_4 and N_2O. Eventually the CFC-12 and CFC-11 concentrations in the NOAA standards will be compared to the set of NIST standards.

7. *Development of Gas Standards for the Next Generation of Automobiles*

***P.M. Chu**, W.D. Dorko, and W.J. Thorn III*

Objective: To develop gas standards for calibrating/validating instrumentation used to measure exhaust from lower emission vehicles in response to clean air regulations.

Problem: The certification of gas standards at levels lower than currently available as SRMs is needed by automobile manufacturers for the characterization of lower emitting vehicles. Development of low concentration standards involves several challenges. Most standards are provided in high-pressure metal gas cylinders where there are storage problems at the lower concentrations. Also, mixtures of reactive gases have stability problems regardless of concentration. To address these issues, new cylinder technology and standards provided by dynamic dilution methods are currently being investigated. Lower concentration standards also challenge current measurement detection limits. As a result, the total uncertainties on the gas standards are higher than the uncertainties desired by the user community. Further characterization of our measurement systems and procedures are underway to reduce the uncertainties.

Approach: Project priorities were established after gaining input from the Automobile Industry/Government Emissions Research (AIGER) Consortium and the Calibrations Gas Panel of the American Automobile Manufacturers Association (AAMA). Three areas were given priority during FY98; 1) Low level nitric oxide gas standards; 2) New California Bureau of Automotive Repair standards (BAR-97) for California's new automobile emission standard; and 3) An on-demand formaldehyde gas standard generator.

Results and Future Plans: A new project has been initiated to develop reliable nitric oxide gas standards in the concentration range between 0.5 μmol/mol and 1.5 μmol/mol. SRM 2629a (nitric oxide, 20 μmol/mol) will be gravimetrically added to specially prepared aluminum cylinders and then diluted using oxygen-free nitrogen. The resulting mixtures will be periodically analyzed at NIST. These mixtures will serve as the infrastructural measurement basis possibly leading in the future to a 1.0 μmol/mol NO standard. The automotive industry has indicated that this standard will be required within a two year time period.

NIST has begun supplying certified concentration values for NO_x as well as NO for nitric oxide SRM certifications. Additionally, NIST is reviewing possible changes to the NTRM protocol document to facilitate the use of NTRMs for future mobile source measurements in place of SRMs. The U.S. EPA at Ann Arbor and the calibration gas panel of the American Automobile Manufacturers Association has provided input for the FY99 revision.

NIST has analyzed the BAR-97 mixtures containing nitric oxide, carbon dioxide, carbon monoxide, and propane. The BAR-97 mixtures will serve as benchmarks for tailpipe emission testing under the U.S. EPA Inspection/Maintenance (I/M) program. These mixtures are technically difficult to measure; however, once the measurements are made, second tier standards can be certified relatively easily. NIST will analyze an additional twenty BAR-97 primary mixtures in FY99.

Ford has conducted tests of the NIST prototype formaldehyde-in-air standard generator. During the performance tests, Ford determined that a formaldehyde output of 150 μmol/mol to 200 μmol/mol (with a maximum variability of ± 3 %) at a flow rate of 2 L/min ± 0.2 L/min is required to meet their sampling conditions. This concentration of formaldehyde is significantly different than the original specifications of 10 μmol/mol formaldehyde delivered at 1 L/min. Although the formaldehyde generator was not optimized to provide formaldehyde at Ford's current requirements, Ford measured the levels of formaldehyde produced by the prototype generator and the results of their measurements agreed with the NIST measurements. Overall, Ford found the system relatively simple to use and that it delivered reproducible levels of formaldehyde. Collaboration between NIST and Ford is ongoing to meet the new concentration and flow specifications.

8. *Investigation of Chromium Diffusion into the Walls of an Industrial Boiler Tank via PGAA with a Focused Neutron Beam*

H.H. Chen-Mayer, R.L. Paul, and D.F. R. Mildner

Objective: To work with scientists from Oak Ridge National Laboratory and the paper industry to map the chromium to iron mass ratios near the surface of a section of a steel boiler tank as part of our support of the NIST Center for Neutron Research National Users' Facility.

Problem: To minimize corrosion, a chromium coating is applied to the walls of some industrial boiler walls that are exposed to harsh chemical environments. The Cr and Fe interdiffuse such that the mass ratio varies as a function of distance from the surface. We are studying this to better understand the process and the resulting enhancement of corrosion resistance. The Cr coating is not expected to be thicker than 0.5 mm. Improved materials could lead to enhanced industrial safety by decreasing premature boiler failures/explosions and to increased efficiency by enabling higher operating temperatures and pressures and reducing downtime.

Approach: The entire sample (about 10 mm x 10 mm x 5 mm, cut from a section of the tank wall) was originally placed in the unfocused beam, collimated with a 20 mm diameter aperture, for normal PGAA analysis. This measurement should have provided bulk information such as the total amount of the Cr in the sample. However, the data interpretation was complicated by the neutron self-shielding effects and gamma ray attenuation by the sample. A more specific analysis at the chromium-steel interface was attempted by performing PGAA with a narrowly focused, neutron beam to determine the Cr to Fe mass ratios at different locations across the interface. We took advantage of the higher neutron intensity, and lower background levels of radiation produced by the neutron bender-focuser for the examination of sub-mm surface regions of a material. We scanned a cross section of the boiler tank wall (1 mm thick) across the focused beam, and obtained the gamma count rates for Cr and Fe as a function of the sample position. We then determined the analytical sensitivities (counts/sec-µg) of Cr (using pressed $K_2Cr_2O_7$ powder pellets) and Fe (using metal foils). The count-rate sensitivities were converted into the mass of Cr and Fe in steel using standard addition techniques.

Results and Future Plans: The mass of Cr and Fe as a function of the sample position relative to the focused beam spot is plotted in Figure 1. A Gaussian distribution was obtained for the Cr signal, with a full-width at half-maximum of 0.89 ± 0.02 mm. This includes the beam width itself, determined separately as 0.84 ± 0.02 mm (FWHM), and the actual Cr distribution, which is derived to be 0.29 ± 0.03 mm (FWHM). The current results indicate that a better spatial resolution, i.e., improvement by approximately a factor of 2 to 5, is required to obtain a diffusion profile that would be useful to the industry. We plan to collimate the focused beam to further improve this spatial resolution. We also plan to undertake additional studies to improve our measurement capabilities in this area with: better characterizing the matrix effects, developing better automation for scanning, and obtaining better reproducibility for the alignment of the sample relative to the focus.

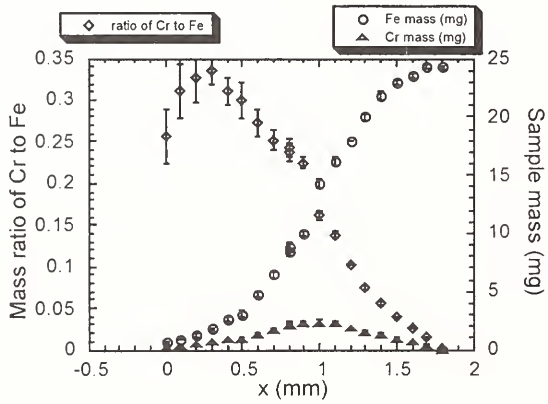


Figure 1. Cr and Fe mass determined by prompt gamma response (right vertical axis) from a Cr-coated steel sample, a section of a boiler tank wall. The horizontal scale is the position of the focused neutron beam scanned in the direction perpendicular to the interface of the sample. Greater abscissae represent positions deeper into the bulk material. The mass ratio of Cr to Fe is also plotted on the left vertical axis. The error bars represent 1 standard deviation of the counting statistics.

9. Development and Evaluation of a Beta Counting Radiochemical Method for Phosphorus Determination

R. L. Paul

Objective: To develop and critically evaluate a radiochemically-based neutron activation analysis method for phosphorus in semiconductor and other advanced materials.

Problem: The presence of phosphorus in metals and semiconductors can affect materials properties. Phosphorus degrades the protective coatings on jet engine turbine blades at mass fractions as low as 1 mg/kg and changes the electrical properties of silicon wafers at mass fractions at the μg/kg level. Although few analytical techniques yield reliable measurement of phosphorus at these levels, radiochemical neutron activation analysis has proven suitable for determination of phosphorus at μg/kg levels or lower.

Approach: A procedure was first developed at NIST for determination of phosphorus in low alloy steels. Modifications of this procedure were later used to measure phosphorus in other materials. Steel samples were irradiated with neutrons at the Center for Neutron Research reactor. Standards, prepared by evaporation of microliter amounts of a standardized phosphorus solution on aluminum foil or MgO, were irradiated with the samples. During irradiation ^{31}P undergoes neutron capture to form ^{32}P, a pure beta emitter with a half-life of 14.28 days. After irradiation the steels were mixed with a few mg of phosphorus carrier and dissolved in a mixture of acids. The solution was passed through a cation exchange resin to remove iron and most other metal ions, and then through tin dioxide to remove As and Ta. The phosphorus was further purified by precipitation as phosphomolybdate and finally as magnesium ammonium phosphate. The final precipitate was filtered, dried, weighed, and the yield (fraction of recovered carrier) determined. A beta proportional counter was used to measure ^{32}P. The precipitate was relatively free of contamination by other nuclides. Comparison of sample count rates and yields with those of standards processed in a similar manner enabled determination of phosphorus mass fractions.

Results and Future Plans: Table 1 shows that the phosphorus mass fractions measured in SRM low alloy steels using the radiochemical neutron activation analysis (RNAA) method are in agreement with certified values within the stated uncertainties. RNAA uncertainties, reported at the 95 % confidence level, are based on measurement replication (N = number of samples analyzed).

Table 1. Phosphorus results by RNAA for SRM steels

SRM No.	N	RNAA (mg/kg)	Certified (mg/kg)
361	6	152 ± 5	140 ± 10
362	17	441 ± 40	410 ± 10
363	6	288 ± 25	290 ± 50
364	6	94 ± 5	100 ± 100

A modified RNAA procedure was also used in the certification of phosphorus in SRM 1548a, *Total Diet*. RNAA is currently being used to certify phosphorus in several alloys of industrial importance. These include a high temperature refractory alloy of cobalt, nickel, chromium, and molybdenum, and an aircraft alloy composed predominantly of nickel and cobalt. Preliminary results indicate that both alloys have < 10 mg/kg of phosphorus. Future plans include measurement of phosphorus in implanted silicon in order to assess the capability of RNAA for certification of phosphorus in a silicon SRM.

Publication:

Paul, R.L., ***"Determination of Phosphorus in steels by Radiochemical Neutron Activation Analysis,"*** J. Radioanal. Nucl. Chem., 234, 55-58 (1998).

10. *Pressurized Fluid Extraction-Micellar Capillary Electrophoresis: A New Forensic Tool for the Analysis of Gunshot Residues*

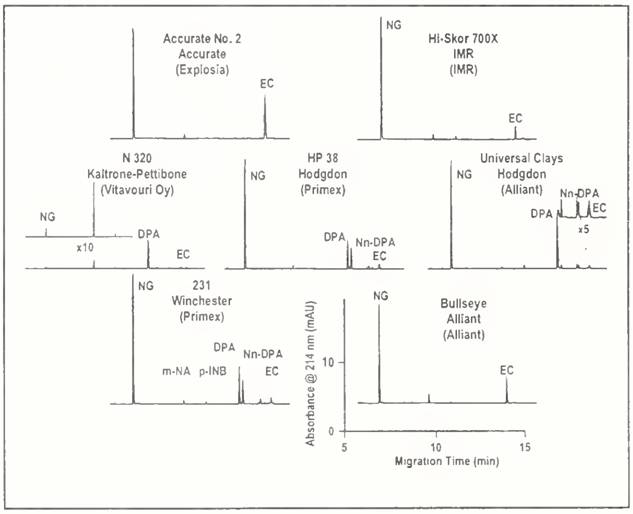
W.A. MacCrehan, K.M. Ricketts, R.A. Baltzersen (George Washington U.), and W. F. Rowe (George Washington U.)

Objective: To critically evaluate a pressurized fluid extraction (PFE)-micellar capillary electrophoresis (CE) method as a forensic tool for analyzing gunshot residues and gunpowder.

Problem: Forensic chemists have a limited number of analytical tools that can be used to investigate handgun and explosives crime involving the use of smokeless gunpowder. Quantitative compositional analysis of gunpowder additives can potentially provide information on the type of gunpowder or ammunition used in a crime. We investigated this possibility by recovering and quantitatively measuring the composition of organic additives in smokeless powder and its post-firing residues. By identifying and quantifying the components of residues for such additives as nitroglycerin (NG), dinitrotoluene (DNT), ethylcentralite (EC), and diphenylamine (DPA), we hope to be able to uniquely distinguish between smokeless gunpowder samples. By the analysis of gunshot residues collected from handgun test firings, we hope to learn what changes are expected in the composition of the residues when compared to the unfired ammunition.

Approach: In a collaboration with the George Washington University's Department of Forensic Sciences, we have been developing a quantitative analysis method for the determination of the additives in gunpowder based on PFE followed by micellar capillary electrophoresis. The conditions for the quantitative extraction of the additives from seven ammunition reloading powders, using neat and solvent-modified supercritical carbon dioxide, are being investigated. Potential losses of the nitrated additives via photo- and reactive decomposition have been minimized in post-extraction sample handling steps. All of the major gunpowder additives can be determined with baseline resolution using CE with a sodium dodecylsulfate micellar agent and UV absorbance detection. We have made a thorough study of 12 candidate internal standards. The new method was used to provide the CE analysis of the test powders presented in the figure. Note that there are differences in the concentration and nature of the additives in these test powders that might be used for identification purposes.

Results/Future/Plans: Armed with this new measurement technique, we are evaluating the compositional changes that might be expected to occur when the ammunition is fired in a handgun. Samples of all seven known powders are being loaded into the most common handgun ammunition types used for criminal activity, 9 mm, 38 and 45 caliber. A contractor, National Technical Services, is test firing 100 rounds of each type into custom-fabricated residue collection boxes. Quantitative comparison of the composition of these muzzle residues to the unfired gunpowder will be made. We hope to determine some rules governing the compositional changes in fired residues relative to unfired gunpowder and whether the changes are dependant on weapon type. These data will help forensic analysts evaluate the certainty with which residues and source gunpowders can be matched.



Publications:

Smith, K.D., McCord, B. R., Mount, K., MacCrehan, W.A., and Rowe, W. F. ***"Detection of Smokeless Powder Residue on Pipe Bombs by Micellar Electrokinetic Capillary Electrophoresis,"*** J. For. Sci. (in press).

MacCrehan, W.A., Ricketts, K. M., Baltzersen, R.A., and Rowe, W.F., ***"Detecting Organic Gunpowder Residues from Handgun Use,"*** in: Proc. SPIE Conference on Investigation and Forensic Science Technologies (in press).

11. Laboratory Research and Interlaboratory Studies Concerning Forensic Application of Hair Analysis

M.J. Welch, B.A. Benner, Jr., K.W. Phinney, and L.T. Sniegoski

Objective: To investigate the use of analysis of human hair for drugs and endogenous compounds for detecting drug abuse and for forensic identification of individuals.

Problem: In recent years much attention has been focused on hair analysis for detection of drugs of abuse since hair retains drugs and other ingested substances for long periods of time. However, a number of controversial issues have not been satisfactorily resolved. One question concerning any new measurement technology is the reliability of the results. Can laboratories accurately identify and measure drugs in hair? Likewise, can drugs found in hair be attributed to ingestion as opposed to external contamination? Studies have shown that the quantity of drug that is deposited into hair varies greatly from individual to individual. Because what gets deposited in hair varies so much and hair treatments vary greatly among people, it may be possible to differentiate among people based upon the patterns of compounds found in their hair, making hair analysis a potential useful tool for forensic purposes.

Approach: NIST has conducted interlaboratory studies with public and private sector participants to evaluate how well laboratories can detect and quantify drugs in NIST-provided hair samples spiked with certain target compounds as well as drug-free hair samples. For differentiating drug use from environmental (passive) exposure, a new approach involving chirality of drugs is being investigated at NIST. Many drug compounds are chiral molecules that exist as mixtures of mirror images, called enantiomers. When ingested, the enantiomers are often metabolized at different rates resulting in an enantiomeric ratio in biological samples that is different from that of the starting composition. Thus, this ratio may provide an indication of the source (endogenous or exogenous) of the drug. Determination of enantiomeric composition of drugs in hair may also be useful in differentiating between legitimate and illegal use of drugs such as amphetamine and methamphetamine whose legal formulations require the use of specific chiral forms.

The increased sensitivity of on-line supercritical fluid extraction-gas chromatography/mass spectrometry (SFE-GC/MS) (which transfers the entire extractable mass to the analytical system) can be exploited for characterizing small samples such as hair samples collected at a crime scene. To investigate the potential of this approach, hair samples from 20 individuals were characterized by SFE-GC/MS in an effort to distinguish among individuals based on the chemical profile of their hair.

Results and Future Plans: Recent interlaboratory studies have found that laboratories with experience in hair analysis generally accurately identify which drugs are present in hair samples. However, quantitative results vary greatly, largely due to differences in the extraction methods used. A planned SRM for drugs of abuse in hair will consist of two different hair materials with a total of eight analytes of interest.

To evaluate forensic applications of hair analysis based on chiral composition, preliminary studies focused on beta blockers (chiral compounds used to treat high blood pressure) in hair samples to establish proof of principle. This study will continue with the assessment of its use for amphetamine applications.

Results from the SFE-GC/MS analysis of hair from different individuals suggest that for most of the samples, consistent chemical profiles were observed from hairs from the same individual and different profiles from hair samples from different individuals. Results of a blind study suggest that SFE-GC/MS may help identify an individual by components extracted from his hair (two of the three samples were correctly identified) and may provide useful information to law enforcement investigators from hair obtained at a crime scene. Planned expansion of the current pool of analyzed hair samples using a more specific sampling strategy may allow better statistical descriptions of similarities and differences among individual chemical profiles and the establishment of relationships between the chemical profiles of hair and the gender, age, and race of the volunteers.

12. Development of a Meat Homogenate SRM

M.J. Welch, K.E. Sharpless, L.T. Sniegoski, C.P. Phinney, L.J. Wood, R.M. Lindstrom

Objective: To develop a meat homogenate SRM to provide quality assurance for the food processing industry. This high fat, high protein material will complement the high carbohydrate (Food Composite, Baby Food, and Infant Formula) and low protein, high fat (Cholesterol in Coconut Oil) SRMs currently available.

Problem: Accuracy in nutritional labeling is important for several reasons. An individual's dietary intake of fats, proteins, carbohydrates, total calories, cholesterol, various minerals, and vitamins has a considerable effect on whether that individual will develop or avoid a variety of conditions that negatively impact his or her health. One must have accurate nutritional information on the foods that he or she consumes to maintain a healthy diet. Large numbers of people are fed through institutional feeding programs, where it is critical that proper nutritional balance be maintained. In addition to the health aspects, there is an economic benefit in accurate labeling to American food processors. The acceptance of their exports in other countries depends upon the government and the consumers of those countries trusting the nutritional information provided. NIST is involved in providing the food processing industry with SRMs to assist them in making accurate measurements of nutrients and to provide traceability to validate their measurements. Representatives from the food processing industry and U.S. government regulators identified a need for a canned meat product reference material certified for individual fatty acids, cholesterol, calcium, sodium, and iron and characterized for the proximates (protein, fat, carbohydrate, ash, moisture, and caloric content).

Approach: A batch of a commercially available canned meat product with a uniform matrix that was high in protein and fat, was specially prepared and canned to serve as an SRM. Certification involved a combination of measurements at NIST and at collaborating laboratories. Analytical laboratories associated with the National Food Processors Association again participated as they did for SRMs 1846 (Infant Formula) and 2383 (Baby Food). The participating laboratories primarily used methods approved by the Association of Official Analytical Chemists for the analytes and proximates of interest. Additional laboratories with expertise in supercritical fluid extractions of fats from foods and in pressurized fluid extractions also participated. At NIST, isotope dilution mass spectrometry was used to measure cholesterol and individual fatty acids; inductively coupled plasma optical emission spectroscopy (ICP-OES) was used for calcium, sodium, and iron; and neutron activation analysis was used to measure the nitrogen content. With the nitrogen content measured at NIST, it is possible to obtain a certified value for total protein in the material based upon the relationship between nitrogen content and total protein as defined by AOAC for meat products.

Results and Future Plans: Based upon statistical analysis of the data, certified values were obtained for six fatty acids, cholesterol, calcium, sodium, iron, and total nitrogen. In addition, reference values were obtained for the proximates (total fat, carbohydrate, protein, water, and ash), calories, a number of other fatty acids, and some additional nutrients.

Representatives from the food industry identified two other food materials for which there are high priority needs for an SRM. One of these would be a high fat, high carbohydrate material; the other would be a high carbohydrate, high protein material. An unsweetened chocolate is an ideal material for the former and a canned spinach is ideal for the latter. Work will begin in FY99 on developing SRMs for these two materials.

13. *Development of SRMs for Toxic Elements in Whole Blood*

***R.D. Vocke**, E.S. Beary, S.E. Long, K.E. Murphy, M.S. Rearick, S. Tutschku, and L.L. Yu*

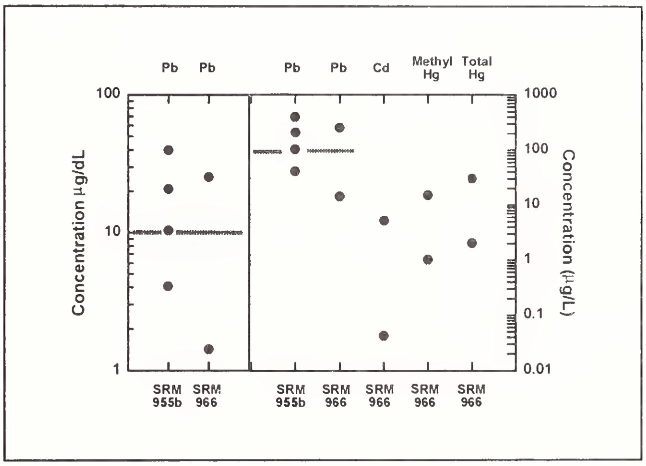
Objective: To provide whole blood reference materials with certified concentration values for selected toxic trace metals.

Problem: SRM 955b, *Lead in Bovine Blood*, is a renewal of a bovine whole blood standard with four different levels of endogenous lead that will provide the traceability link for accuracy of blood lead measurements by public health laboratories. These levels were chosen to help the analytical community accurately meet decision point criteria in the management of pediatric lead poisoning. For example, pediatric lead levels less than 10 μg/dL (while elevated above baseline levels) are currently considered normal and require no remedial action while levels greater than 20 μg/dL require medical intervention.

SRM 966 is a new bovine whole blood standard with two different levels of organically bound lead, spiked cadmium and spiked mercury, both methyl (MeHg) and inorganic forms (Hg^{++}). It was developed to address needs for a whole blood reference material that contains baseline levels as well as elevated levels of these toxic heavy metals. The large number of participants (U.S. as well as foreign) in proficiency testing programs utilizing sample of this type is indicative of continuing interest in workplace and general public health monitoring for MeHg and Cd in blood. At present, only proficiency samples with consensus cadmium values exist as standards. A large number of prestigious organizations in the human health monitoring arena (e.g., the Center for Disease Control (CDC), National Institute of Environmental Health and Safety, EPA, and the World Health Organization) have expressed a need for biological SRMs certified for dietary mercury as MeHg.

Approach: The base material for these SRMs was prepared for NIST by the CDC who collected six pools of blood from cows that had been dosed with lead nitrate ethylene-diamine-tetra-acetic acid (EDTA) was added to each lot to prevent micro-clotting.) One pool was spiked with methyl mercury (as iodide), inorganic mercury, and inorganic cadmium. The other five pools were unspiked. All pools contained different levels of endogenous lead. Four of these pools became the base material for SRM 955b while the remaining two pools were used for SRM 966. Certification of the analytes was generally be done by multiple methods, except where a definitive method existed. Value assignment of the Pb and Cd contents of these SRMs were based on isotope dilution ICP-MS, with confirmatory analyses by externally calibrated high-resolution-ICP-MS measurements. Value assignment for MeHg and Hg^{++} were done by GC-atomic emission spectroscopy and confirmed with HR-ICP-MS.

Results and Future Plans: The data for the different standards and their respective analytes are shown below. The indicated line for the lead values is the current CDC mandated level for medical intervention in cases of pediatric lead poisoning. Note that the concentration units of the left box are μg/dL while the right box has units of μg/L. The ranges of analyte concentrations in these two reference materials span five orders of magnitude.



A select group of international experts will analyze SRM 966 for Cd and speciated Hg values in a small round robin analytical exercise prior to its release as an SRM to assess the degree of comparability of such measurements worldwide. CDC remains committed to supporting the NIST effort of providing a definitive accuracy base for toxic metals in blood analyses through future collaborative endeavors.

14. *Spectral Reference Database Developed to Support Open-Path FT-IR Measurement of Environmental Contaminants*

P.M. Chu, G.C. Rhoderick, F.R. Guenther, and W.J. Lafferty (Optical Technology Division, PL)

Objective: To develop a quantitative reference spectral database to support open-path Fourier transform infrared (FT-IR) measurements of chemical emissions and hazardous air pollutant molecules.

Problem: With the recent developments in FT-IR spectrometers it is becoming more feasible to place these instruments in field environments. As a result, FT-IR techniques offer the possibility of fully automated real-time quantitation of many analytes and FT-IR methods have great potential as an analytical tool. Recently, the U.S. Environmental Protection Agency (US EPA) has developed protocol methods, TO-16, for emissions monitoring using both extractive and open-path FT-IR measurements. Depending upon the analyte and the analyte matrix, approximately 100 out of the 189 hazardous air pollutants (HAPs) listed in the 1990 US EPA Clean Air Act amendment (CAAA) can be measured with FT-IR.

Quantitative measurements from field spectra require an accurate reference spectral database. A user can generate quantitative reference spectra; however, this can be a time consuming and costly process. Comparisons of reference spectra from the available quantitative collections show that the agreement of reported intensities is frequently ± 10 % or worse. Impurity bands present in these reference spectra can also interfere with the interpretation of field results.

Approach: Primary standard gas mixtures (PSM) are prepared at NIST using starting materials of assessed purity and procedures that minimize contamination. The final concentrations of these standards are verified by gas chromatography using several independently prepared calibration mixtures. The PSMs of various known concentrations are each continuously flowed through the sample cell and data averaging is initiated after a steady-state spectrum is obtained. A research grade FT-IR spectrometer is used to obtain the spectra at a nominal resolution of 0.12 cm^{-1}. For each compound, the absorption coefficient spectrum was calculated using nine transmittance spectra and the Beer's law relationship. Comparisons of gas standards prepared by NIST and the National Physical Laboratory (NPL), UK and comparisons of spectral data from NIST-prepared samples by NPL have been used to assure the quality of the data.

Results and Future Plans: Absorption coefficient data for 21 HAPs on a US EPA priority list have been published as the NIST Standard Reference Database (SRD) 79, version 1.00. The data are stored on a CD-ROM in the standard JCAMP-DX format to enable universal access to the data. The initial 0.12 cm^{-1} resolution data have been processed to generate data at a number of different resolutions and apodizations, providing the users with data that more closely match their experimental parameters. The uncertainties in the absorption coefficient data were estimated from the linear regressions of the transmittance data and considerations of other error sources such as the non-linear detector response. For absorption coefficient values greater than 1×10^{-4} $(\mu mol/mol)^{-1}$ m^{-1}, the average relative uncertainty is 2.2 %. A digital signature accompanies each data file, allowing users to ensure the integrity of the data file and traceability to NIST.

This quantitative infrared database is an ongoing project at NIST. Additional spectra will be added to the database as they are acquired and updates to the NIST SRD 79, version 1.00 will be available over the Internet. Current plans include continued data acquisition for the compounds listed in the CAAA as well as additional compounds that contribute to global warming and ozone depletion.

Publications:

Chu, P.M., Guenther, F.R., Rhoderick, G.C., and Lafferty, W.J., ***"NIST Standard Reference Database 79,"*** Version 1.0, (October 1998).

Chu, P.M., Guenther, F.R., Rhoderick, G.C., and Lafferty, W.J., ***"The NIST Quantitative Infrared Database,"*** NIST Journal of Research (in press).

15. *Measurements to Evaluate and Optimize Sewage Wastewater Chlorination Processes*

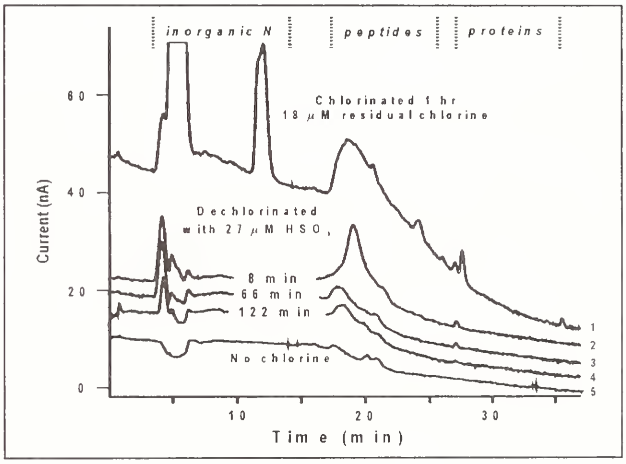
W.A. MacCrehan, G. Helz (U. Maryland), R.H. Jameel, and M. Bedner

Objective: To minimize the environmental impact of chlorine sewage wastewater disinfection by developing and applying new measurement methods for the determination of the organic compounds that contribute to "residual chlorine."

Problem: Over 40 billion gallons/day of sewage wastewater is discharged into the environment by U.S. municipal wastewater treatment facilities. Human health and the environment are protected from the toxic effects of pathogenic bacteria and viruses by disinfection, largely (>90 %) by the addition of chlorine or hypochlorite to achieve an excess "residual chlorine." However, to mitigate the toxicity of chlorine, many treatment facilities "dechlorinate" with sulfur dioxide or sulfite. Even so, chlorinated/dechlorinated effluents have shown unexplained residual toxicity to aquatic life. Although the US EPA has established a target "criterion" of 11 ng/g as Cl_2 for discharge, there are no analytical techniques that can make reliable measurements at that level. Environmental researchers have speculated that slow dechlorination of organic chloramines contributes to the observed wastewater toxicity, but this has not been measured in the laboratory.

Approach: In collaboration with the University of Maryland's Water Resources Research Center, we have been developing an analytical method that can measure and discriminate between inorganic and organic chloramines in wastewater. The method measures organic chloramines using gradient-elution reverse-phase liquid chromatography. Chloramines are detected using a post-column reaction with iodide in manner that is similar to the measurement of total residual chlorine by titration. Our LC determination is completed by amperometric reduction of the iodine formed. The figure shows the determination of the organic products that persist after chlorination/dechlorination of process wastewater from a treatment facility in Beltsville, MD. Trace 1 shows the organic chloramines after the initial chlorination; trace 2 shows the chloramine content after 8 minutes of dechlorination time with sulfite; trace 3 after 66 minutes of dechlorination; and trace 4 after 122 minutes. Trace 5 shows the selectivity of the detection scheme; with no detectable compounds found for wastewater that had not been treated with chlorine. Based on retention and kinetic dechlorination data, the chromatographic peaks at 19 and 27 min are likely to be chloramines of peptides and protein, respectively.

Results/Future Plans: The achievable detection limit of the current method is within a factor of two of the EPA criteria. We hope to improve the method by developing an LC separation optimized specifically to provide high selectivity for the measurement of peptides and proteins and by improving the detection sensitivity by identifying better post-column reaction chemistries/conditions and by exploring other direct detection modes. We have also initiated experiments to identify specific peptides and protein chloramines in the wastewater. An important future NIST role will be to support measurements of these highly reactive chloramines by the development of calibration approaches and by providing SRMs for wastewater treatment.



Publications:

MacCrehan, W.A., Jensen, J.S., and Helz, G.R., ***"Sewage Organic Chlorination Products That Are Slowly Dechlorinated by Sulfite,"*** in: Proc. Disinfection '98 Symposium, Haas, C.N and Connell, G.F., eds., WEF Publications, Alexandria, VA, pp. 91-97 (1998).

MacCrehan, W.A., Jensen, J.S., and Helz, G.R., ***"Detection of Sewage Organic Chlorination Products That Are Resistant to Dechlorination with Sulfite,"*** Environ. Sci. & Technol. (in press).

16. *Development and Production of an Urban Air Particulate Matter on Filter SRM*

R. Zeisler, S.F. Heller-Zeisler (U. Maryland), and J.M. Ondov (U. Maryland)

Objective: To collect a contemporary fine particle, $PM_{2.5}$ (particulate matter smaller than 2.5 µm aerodynamic diameter) aerosol material from an urban site and produce a filter-based SRM to support EPA's national aerosol monitoring program and the development of new $PM_{2.5}$ air quality standards.

Problem: Investigations into the amounts and composition of air particulate are currently carried out in virtually every country. The investigations in the U.S. are focusing on the particularly high risk factors associated with the fine fraction ($PM_{2.5}$) of aerosols. The primary techniques for trace element analysis are based on nuclear physics principles (PIXE, XRF, NAA, etc.) due to their suitability for multicomponent determinations on the small samples typically available. However, few appropriate quality assurance materials are available to support this work. SRM units of reference material distributed on filters are most suitable for this community. To assist in effective measurement and control of $PM_{2.5}$ aerosols in an economically sustainable way, NIST is developing this new class of SRMs.

Approach: Air particulate matter corresponding to the $PM_{2.5}$ fraction was collected at an established EPA monitoring site in an urban residential area in Baltimore MD. An air sampling system separates fine particles (at a calculated cut-off point of 1.5 µm) with a cyclone separator and deposits them onto an 0.5 m^2 array of 20 cm by 25 cm Teflon membrane filters at a rate of approximately 1 g of $PM_{2.5}$ aerosol per day.

The $PM_{2.5}$ aerosol is removed by ultra-sonication from the Teflon membrane filters and suspended in water. Aliquots of the suspension are filtered through 47 mm diameter polycarbonate filter membranes with 0.4 µm pore size to form the SRM units. The $PM_{2.5}$ aerosol covers 10 cm^2 on each filter at an area density of 0.5 $mg \cdot cm^{-1}$.

The composition of the collected $PM_{2.5}$ aerosol, as well as the composition of the deposited $PM_{2.5}$ aerosol, are being determined by INAA and other techniques. The homogeneity of the SRM units will be measured by gravimetry and INAA; microhomogeneity of the deposited $PM_{2.5}$ aerosol will be determined with microscopic and micro-analytical techniques.

Results and Future Plans: Four collection cycles during late summer of 1998 resulted in the deposition of 20 g of $PM_{2.5}$ aerosol to be used for this SRM. In initial tests to ensure the suitability of the collected material, the $PM_{2.5}$ aerosol exhibited the following mass fractions of selected elements measured by INAA and AAS: Al 3.3 %, V 0.16 %, Cr 2.5 %, Mn 0.36 %, Ni 1.5 %.

After the homogeneity of a series of test filters has been assessed, the particulate on filter SRM units will be produced using the collected material. The initial production of these test filters provided opportunities for improvement of the previously developed and applied small-scale production process for a prototype reference material. Automated processing of the deposit on filters and continuous monitoring of the particle density in the $PM_{2.5}$ aerosol water based suspension will enable NIST to produce and certify a high quality SRM.

Reference:

Heller-Zeisler, S.F., Fajgelj, A., Bernasconi, G., A Tajani, R. Zeisler, "***Examination of a Procedure for the Production of a Simulated Filter Based Air Particulate Matter Reference Material,***" Fresenius' J. Anal. Chem., 360, 435-438 (1998).

17. Development of an Arsenic Implant in Silicon SRM for the Semiconductor Industry

R. M. Lindstrom and D. S. Simons (Div. 837)

Objective: To certify the amount of arsenic in silicon for an SRM to calibrate and/or validate industrial ion-implantation processes.

Problem: The secondary-ion mass spectrometry (SIMS) community in the U.S. recently undertook a round-robin study to calibrate the implanted dose of arsenic in silicon by consensus. For this exercise several 200 mm silicon wafers were implanted with arsenic with high uniformity by a state-of-the-art implanter. Exercise results showed that variations in dose determination among laboratories were as high as 30 %, reflecting primarily the dose errors of in-house standards used by participants. This demonstrates the need for a common reference material to improve interlaboratory reproducibility. Furthermore, SEMATECH recently listed SRM implants of phosphorus and arsenic in silicon as high-priority industrial needs.

Approach: A Standard Reference Material (SRM 2134) was produced at NIST, using a wafer from the SIMS round-robin comparison. Instrumental neutron activation analysis was used as a reference technique [1] for certification of the arsenic implanted dose. Ten analytical specimens were systematically selected from the array of 221 chips into which the wafer was cut. The analytical procedure was designed to compensate for all systematic errors that are well understood, and reveal any remaining unrecognized ones. Two independent As standards were prepared from high purity materials and each sample and standard was counted at least twice. Because the half-life of ^{76}As is only 26 hours, the sample set was measured within three days so that the activity of each sample would be great enough to be precise, and the decay correction would be small enough to be accurate. The mean precision due to counting statistics was 0.25 % (1σ). A recent determination [2] of the half-life of ^{76}As (1.0778 d ± 0.0020 d) was used in the calculations, in preference to the 1972 value (1.097 ± 0.003 d) quoted in the current *Table of Isotopes* [3]. The difference between these two half-lives corresponds to a difference of 2.8 % in the decay correction at the end of the 2.5-day counting period. In this work, we checked the half-life by following the decay of eight standards for as long as twelve half-lives. Our mean value was 1.086 d (s = 0.003 d).

Results and Future Plans: The observed As concentrations of all samples agreed within the analytical uncertainties, indicating no significant heterogeneity as a function of sample position on the original wafer. For the ten samples, the average ratio of the first measurement to the second was 0.992 (s = 0.008), showing that the corrections for decay and dead time were in control. Two samples were rinsed with 10 % HNO_3 between counts: no difference between the two measurements was detectable, showing that no significant amount of As was easily removable from the surface. Neither of the silicon blanks (unirradiated portions of a similar Si wafer) showed any measurable As. The position of the samples in the irradiation stack was insignificant indicating no significant errors due to neutron flux drop-off, neutron absorption, or neutron scattering. This was expected: the calculated transmission of thermal neutrons through five Si layers 0.7 mm thick is 99.7 %. The overall weighted mean was 91.06 ng As per specimen (s = 0.37 (0.40 %), n = 10). The SRM certificate is in preparation for issue. In the future, we plan to complete analytical methods development and then to certify a phosphorus implant in silicon SRM, and a titanium nitride thin film on silicon SRM, as requested to complete the current highest priority requests from SEMATECH.

Publications:

Grasserbauer, M., ***"Critical Evaluation of Calibration Procedures for Distribution Analysis of Dopant Elements in Silicon and Gallium Arsenides,"*** Pure & Appl. Chem. 60 (1988). 438-444.

E. P. Mignonsin, ***"Determination of Half-lives by Gamma-Ray Spectrometry: Improvement of Procedure and Precision,"*** *Appl. Radiat. Isotop.* 45 (1994), 17-24.

Firestone, R.B., and Shirley, V.S., ***"Table of Isotopes,"*** 8th ed., Wiley, New York, 1996.

18. *In-situ Measurement of Lithium Movement in Thin Film Electrochromic Coatings*

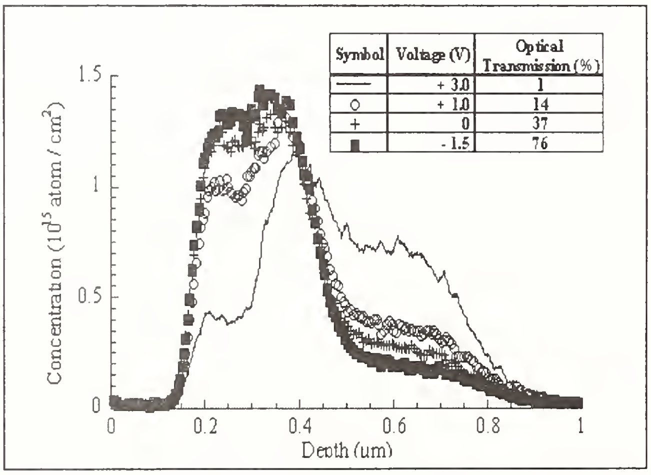
G.P. Lamaze and H.H. Chen-Mayer

Objective: To measure lithium concentration and mobility in thin multilayer electrochromic (EC) films.

Problem: Electrochromism has been used in controlling the optical characteristics of glass surfaces by a simple switch of voltage. This technology has great potential for both energy conservation and for esthetic control of the environment. Although electrochromism has been studied intensively for decades, basic coloration and transfer mechanisms have not been confirmed due to a lack of analytical data performed on complete, active electrochromic devices. Thin multilayer EC coatings exhibit significant optical density changes when a low voltage is applied across the structure. The optical response derives from an electrochemically-induced redox reaction involving transfer of lithium ions between an electrochromic electrode (tungsten trioxide) and a counter electrode (CE) layer. The determination of the amount of the transfer was particularly challenging in that the lithium mobility must be assessed *in-situ* in active devices.

Approach: The samples are placed in a cold neutron beam at the Center for Neutron Research reactor. The lithium profiles are deduced based on the measurement of the energy of alpha particles from the ^{6}Li(n,α)^{3}H reaction. The alpha particles pass through the layers and lose energy through interactions with the matrix. The residual energy of the particles is measured with surface barrier detectors. Because the starting energy of the alpha particles is fixed, the energy loss is obtained by a simple subtraction. This measured energy loss, when combined with a calculated energy loss per unit depth (dE/dx), provides the depth of the originating lithium nucleus. In this case, *in-situ* measurements were taken with different bias voltages on the film layers. The bias causes the lithium to migrate between different layers while changing the optical transparency of the film. To assure that the transparency of the device was actually changing, a simple apparatus to measure the light transmission was installed in the vacuum chamber. As the voltage on the layers was varied, the optical transmission was measured simultaneously with the measurement of the lithium profile. The profiling technique is non-destructive allowing repeated cycling of the device.

Results and Future Plans: The figure shows the profiles for these measurements and the results of the optical measurements. The indicated optical transmission numbers are relative to that without films between the light source and the receiver. Correlation of the measured optical transmission with the quantity of lithium transferred from the CE to the tungsten oxide layer is apparent. The small squares represent the device at -1.5 V in its transparent state and show that most of the lithium is concentrated in the CE and the ion conductor (IC). The small circles represent the device at 1 V while the solid line represents the device in its fully "darkened" state. In this darkened state, the profile shows that lithium is primarily localized in the IC and the WO_3 though some lithium remains "bonded" in the CE. Among the information gained in this study was knowledge of critical process chemistry, migration of lithium into inactive layers, and lithium loss from active layers during accelerated life tests.



We plan to continue measurements on EC films to determine which material properties yield the best devices. We also plan to apply the neutron depth profiling (NDP) technique to study the characteristics of electrical storage batteries containing lithium single-ion conductor systems. The purpose of this study would be to obtain information needed to improve the performance of such batteries. In particular, NDP would be used to determine the lithium distributions in an effort to understand the reasons for such current problems as: charge capacity loss with cycling; lower than theoretically attainable maximum charging and discharging current densities in batteries.

19. *Biochemical Interactions in Imprinted Plastic Microfluid Devices*

L.E. Locascio

Objective: To study biochemical interactions with plastic surfaces in imprinted plastic micro-analytical devices.

Problem: Micro-analytical technology is gaining commercialization momentum due to the greatly reduced cost of using plastics. One current disadvantage of using plastic substrates is that many of the basic properties of plastics necessary for their successful application in bioanalytical separations have not been characterized. This lack of fundamental information has limited the broad use of plastics in electrophoretic and chromatographic separations in microanalytical systems.

Approach: Use of plastic substrates required for applications in bioanalytical micro-separations was studied using a simple, low-cost method for device fabrication in plastics, a low-temperature imprinting techniques. Several characteristics of imprinted plastic microchannels are currently under investigation including parameters affecting the electroosmotic (EO) flow and characteristics of protein absorption. EO flow is the bulk fluid flow that occurs in microchannels under the influence of an electric field and is strongly influenced by surface charge. Since the EO flow rate is directly related to the native charge on the walls of the plastic microchannels, changes in EO flow in the presence of protein are indicative of wall adsorption. This information is useful in choosing the appropriate plastic substrates for bioanalytical separations.

Results/Future Plans: EO flow rates were measured in three different plastic substrates, acrylic, polystyrene, and copolyester, and found to be 0.07, 0.05, and 0.15 cm s^{-1} (electric field = 300 V cm^{-1}), respectively. The direction of the EO flow indicated that the total surface charge in each of the plastic channels was negatively charged. The non-specific adsorption on the walls of the acrylic and polystyrene channels was significant, and caused reductions in EO flow by more than 50 %.

Figure 1 shows the results of an immunoassay separation performed in the microanalytical device. Fluorescent peaks were monitored using a photomultiplier tube mounted on a fluorescence microscope viewing the microchannel. The peaks are associated with a fluorescently-labeled morphine derivative used as the label in a competitive homogeneous immunoassay. Morphine antibody was mixed with sample morphine and a known quantity of fluorescently-labeled morphine. Electrokinetic injection and separation using an electric field resulted in two resolved peaks with one peak representing labeled morphine bound to antibody, and the other, unbound labeled morphine. The seven sequential injections shown in Figure 1 (each showing two separate peaks) should have been identical. However, wall adsorption effects caused irreproducible measurements, as well as shifts in retention times caused by flow rate fluctuations. The reproducibility of sequential injections could be improved by pre-priming the device with several injections of the sample. A successful immunoassay for morphine was demonstrated in an imprinted plastic micro-channel device with electrophoretic separation of components. After priming the system with four test injections, the analytical data showed two well-resolved peaks with retention times of 14.0 s and 31.0 s. For three injections of sample, the relative standard deviation for peak height for the two peaks were 1.3 % and 5.1 %. Future work will include the characterization of other commercially-available plastics, and the evaluation of cell adsorption and lysis in these substrates

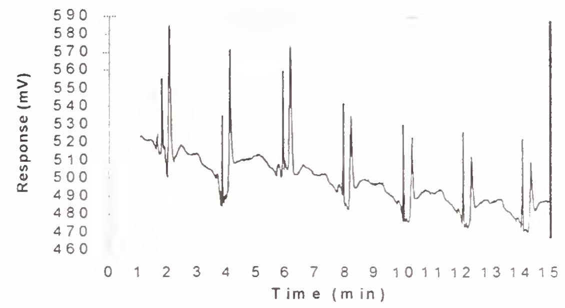


Figure 1. Seven injections of morphine antibody and labeled morphine.

Publications:

Martynova, L., Locascio, L.E., Gaitan, M., Kramer. G.W., Christensen, R.G., and MacCrehan, W.A., *"Fabrication of Plastic Microfluid Channels by Imprinting Methods,"* Anal. Chem., 69. 4783-4789 (1997).

20. Glow Discharge Optical Emission Spectrometry for the Determination of Non-Metals in Solid Samples

M.R. Winchester

Objective: To develop glow discharge optical emission spectrometry (GD-OES) as a method for the quantitative determination of non-metallic elements in solids.

Problem: Quantitative determination of non-metallic elements in solids is an important analytical problem in a wide range of technologies. One reason is that these elements often dramatically affect materials properties - even when present at low levels. Unfortunately, the non-metals are also among the most difficult of all atomic analytes to determine quantitatively. Even though methods for their determination exist, in many cases, state-of-the-art analytical chemical metrology has not kept pace with the technological requirements. Consequently, there is a need for better analytical methods to be developed.

Approach: GD-OES is an established method for the elemental analysis of bulk metals directly in the solid state, and has become popular in European and Japanese industries for routine quality control. Traditionally, GD-OES has been used primarily for the determination of transition elements, but has recently shown promise for the determination of non-metallic elements, as well. At NIST, GD-OES is being developed as a method for the routine quantitative determination of non-metals. The method should provide a suitable alternative to existing methods, especially for selected difficult problems within U.S. industry. In order to enable this work to be conducted with maximum effectiveness and efficiency, a CRADA has been established with LECO Corp. (St. Joseph, MI), the only U.S. manufacturer of GD-OES instrumentation. The collaboration formally began on January 1, 1998.

Results and Future Plans: Research during FY98 concentrated on the determination of C, P, S, and Si in grey cast iron. From an economic viewpoint, grey cast iron is very important, accounting for 43.4 % of all metal products cast in the U.S. in 1995. The U.S. metalcasting industry produced $23 billion worth of goods the preceding year. (From: "Beyond 2000: A Vision for the American Metalcasting Industry," September, 1995) Unfortunately, the quantitative determination of these elements in grey cast iron is virtually impossible with spark OES, the traditional workhorse method of the U.S. metals industry, due to the presence of graphitic C. This has forced industry to maintain multiple methods, in order to perform the full range of elemental determinations necessary for complete quality control.

In NIST research conducted this year, a GD-OES method for the determination of C, P, S and Si in grey cast iron was developed, and three grey cast iron Certified Reference Materials (CRMs) were analyzed. Specifically, white cast iron CRMs were used as calibrants, because very few grey cast iron CRMs are available. In order to correct for the analytical bias that resulted from the matrix mismatch between samples and calibrants, type standardization, a technique sometimes employed in spark OES, was applied. Results showed good agreement with certified values, with the relative biases averaging 1.9 %, 0.7 %, 2.2 %, and 0.9 % for C, P, S, and Si, respectively. From the perspective of U.S. industry, the ability to determine these elements quantitatively using GD-OES relieves the need to maintain multiple analytical methods, providing an economic benefit.

Future GD-OES work at NIST will be concerned with other difficult analytical problems of importance to U.S. industry. One example is the determination of N in alloys containing Ti. In such cases, N tends to be chemically bound to Ti, resulting in analytical bias for spark OES. Because of the fundamental nature of analytical signal production in glow discharge, GD-OES should not suffer from this problem.

Publication:

Winchester, M. R. and Maul, Charles, ***"On the Determination of C, P, S, and Si in Grey Cast Irons Using Glow Discharge Optical Emission Spectrometry,"*** J. Anal. At. Spectrom., 12, 1297-1305 (1997).

21. *Traceability in Chemical Spectrophotometry*

J.C. Travis and G.W. Kramer

Objective: To enhance the availability of NIST traceable standards for spectrophotometry by leveraging NIST photometric accuracy into the commercial sector.

Problem: NIST has produced SRMs for calibrating the wavelength scale and verifying the absorbance accuracy of UV/visible chemical spectrophotometers for several decades. The NIST production capacity is rapidly becoming insufficient to meet the demand, and a recently developed program to leverage NIST measurement capability through the private sector is being adapted for these standards.

Approach: A NIST Traceable Reference Material (NTRM) is a reference material produced by a commercial supplier with a well-defined traceability to NIST. This traceability is established via criteria and protocols defined by NIST that are tailored to meet the needs of the metrological community to be served. The NTRM concept was established to allow NIST to respond to the increasing needs for high quality reference materials with constant human and financial resources. Reference material certifiers adhering to these requirements are allowed to use the "NTRM" trademark to identify their product.

A series of workshops was held at NIST to formulate the concepts of the first spectrophotometric NTRM program. Technically knowledgeable representatives of spectrophotometer manufacturers, manufacturers of optical filters/cuvettes/liquid reference materials, relevant measurement services laboratories, and end users of spectrophotometric standards from user communities that include clinical laboratories, pharmaceutical manufacturers, and chemical manufacturers attended the workshop. From the beginning, the workshop participants supported the NIST suggestion to develop NTRM neutral density glass absorbance standards first and then eventually to expand the NTRM spectrophotometric standards into other areas.

Results and Future Plans: The first NTRMs for chemical spectrophotometry will be on the market in about one year, and will be modeled on NIST SRM 930e and SRM 1930, neutral density glasses (in a cuvette-simulation format) certified at five wavelengths in the visible spectral region and spanning absorbances between 0.3 and 2.0. The expanded uncertainties for the certified values will be kept close to those of the corresponding NIST standards by reducing the NTRM recertification period to one year, which will be compatible with the renewal cycle of many industrial QC protocols.

Initially, NTRM neutral density glass absorbance filters will share the nominal transmittance levels and certification wavelengths of SRM filters. This restriction may eventually be eased to permit the production of NTRM filters at other nominal transmittances and wavelengths within the ranges spanned by SRM filters. Within the current framework, a given certifier may choose to offer fewer transmittance levels and/or certification wavelengths than NIST offers, but may not offer more of either.

Other NTRM filter reference materials will follow for wavelength calibration and UV absorbance verification. For all of these reference materials, the certifying laboratories will be accredited through the NIST-based National Voluntary Laboratory Accreditation Program (NVLAP) and will maintain periodic comparison measurements with the National Reference Spectrophotometer in the Analytical Chemistry Division of NIST.

Publication:

Travis, J.C., Kramer, G.W., Smith, M.V., and Choquette, S.J., ***"Challenges in Providing SRMs for Chemical and Pharmaceutical Process Analysis,"*** Analytica Chimica Acta, 374, (in press) (1998).

22. *Development of a Near Infrared Transmission Wavelength Standard*

S.J. Choquette, J.C. Travis, and C. Zhu (Optical Technology Division, PL)

Objective: To develop a wavenumber/wavelength (x-axis) calibration standard for transmission spectrometers operating in the near infrared (NIR) spectral range from 10 000 cm-1 (1000 nm) to 5000 cm-1 (2000 nm).

Problem: The NIR spectra of organic analytes are composed of overtone and combination bands from the primary vibrational transitions found in the mid-infrared. The extinction coefficients of these bands are 10 to 10 000 times lower than those of the mid-infrared bands. This allows NIR spectroscopy to be used directly with native matrix samples, mostly without sample preparation, and typically in real-time. A growing number of chemical industries, especially agriculture, food, and pharmaceutical manufacturing, are looking to the NIR for methods to replace traditional spectroscopic and wet chemical techniques. Because NIR bands are broad and overlap, full-spectrum, "chemometric" models are used to correlate the chemical composition of the desired analyte with its NIR spectrum. A critical requirement for NIR determinations is the calibration of the wavelength axis. NIST currently offers two NIR wavelength SRMs, SRM 1920 and SRM 2517. Neither of these is suitable for the calibration of NIR spectrometers operating in transmission throughout the entire NIR spectral range.

Approach: Based upon results of an interlaboratory study, a glass optical filter was designed containing several rare earth oxides to provide well defined absorbance features from 10 000 cm^{-1} to 5000 cm^{-1}. The filter glass contains 3.00 mole % Ho_2O_3, 1.30 mole % Sm_2O_3, 0.68 mole % Yb_2O_3, and 0.47 mole % Nd_2O_3. These concentrations were chosen to yield peak absorbances between 0.2 and 0.6 with 1.5 mm thick filters.

Results/Future Plans: Figure 1 shows the spectra of this new material, with its well-defined features throughout the NIR spectral range. The initial lot of 100 filters of SRM 2035a were batch certified with a Fourier Transform NIR spectrometer. The 95 % confidence interval for the peak locations is better than 0.3 cm^{-1} for all seven certified peaks. Because we were not able to obtain high quality wavelength measurements, the certified values on these filters are in wavenumbers and only reference values could be assigned to the wavelength locations of the peaks. Future work will include certifying subsequent filter lots in wavelength on our newly acquired NIR dispersive spectrometer and evaluating the use of these filters in a diffuse reflectance mode.

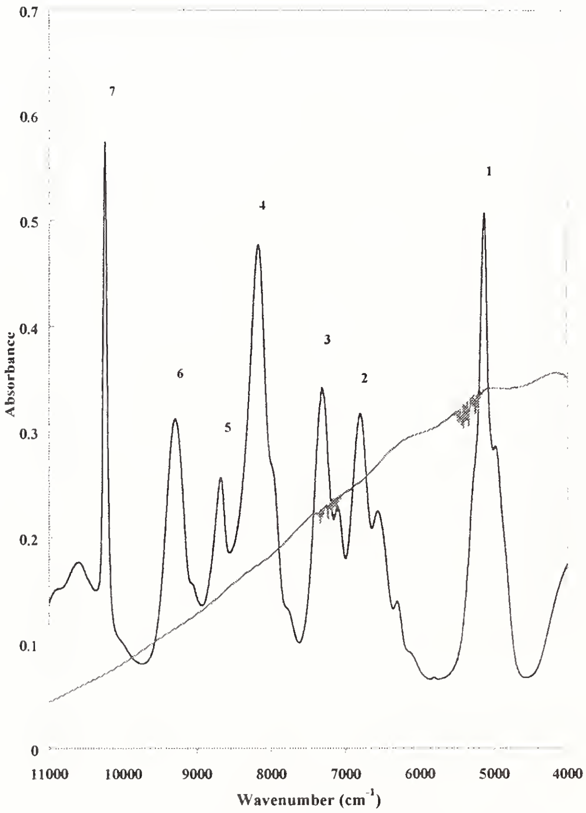


Figure 1. Near infrared spectrum of SRM 2035 and single beam air reference spectrum

Publication:

Choquette, S.J, Travis, J.C., Duewer, D.L., ***"SRM 2035: A Rare Earth Oxide Glass for the Wavelength Calibration of Near Infrared Dispersive and Fourier Transform Spectrometers,"*** in: Proc., SPIE, Optical Diagnostic Methods for Inorganic Transmissive Materials, 3425, pp. 94-102 (1998).

23. NIST Commences Accreditation/Oversight of Proficiency Test Study Providers for EPA/States Water Programs

***R.M. Parris** and W.E. May*

Objective: To establish a system under which private sector companies and interested states can be accredited by NIST to provide proficiency testing (PT) that meets the needs of EPA and states to those laboratories testing drinking water and wastewater for regulated chemical, microbial, and radiochemical, parameters.

Problem: Since the 1970's, EPA has conducted semiannual proficiency testing to assess the competence of over 6,000 public and private sector laboratories to conduct analyses required by the Clean Water and the Safe Drinking Water Acts. At the end of 1998, the cost-free provision of these services will be phased out and replaced by a multi-provider system in which interested states and private companies will provide these PT services on a fee-basis. Mechanisms and tools to provide appropriate government oversight of these programs are needed.

Approach: In a government-private sector partnership, NIST is working with the EPA, States, and other public and commercial entities to establish appropriate oversight of this new effort to externalize and improve the nation's environmental laboratory PT programs. Under this arrangement:

EPA:
- provides NIST with support to develop a program for private sector/state provision of PT studies, and
- works with States and NIST to assure that the program developed for 1) preparing, value-assigning and distributing PT samples and 2) evaluating the quality of the Environmental Testing Laboratory data is sufficient to support national/state water program needs

NIST:
- develops and manages program for accrediting private sector water PT study providers,
- establishes and maintains SRMs to support the program, and
- conducts blind sample audits of the commercially supplied PT samples on an ongoing basis as part of our QA responsibility for the program.

PT Study Providers:
- develop, manufacture, value-assign, and distribute PT samples,
- score results of Environmental Testing Laboratory analyses,
- report result to participants, EPA, NIST, States, and appropriate accrediting authorities, and
- maintain accreditation through NIST NVLAP

Results and Future Plans: Since EPA announced the externalization of the EPA water performance evaluation studies with NIST accreditation of private sector study providers, extensive discussions among the various stakeholders ensued as the roles/requirements of the program were delineated and concerns addressed. A NIST handbook describing the technical requirements of this accreditation program was drafted, presented for comment at January 16, 1998 public meeting, and issued as a revision. NIST NVLAP is now accepting applications for accreditation in this new field, Providers of Proficiency Testing, for the provision of chemistry and microbiology PT studies as described in EPA's "National Standards for Water Proficiency Testing Studies: Criteria Document" (US EPA, August 20, 1998 Version). NVLAP program designations for providers of radiochemistry PT studies will be added after the EPA requirements for these studies have been delineated by US EPA in its criteria document.

NIST has begun producing primary benchmark materials such as SRMs for those parameters not covered by existing SRMs to provide the infrastructure needed by NIST to audit the commercially supplied PT samples and to assist providers in value-assigning their PT materials.

24. Ensuring International Traceability for pH Measurements

K.W. Pratt

Objective: To strengthen the framework for international traceability in pH metrology through two separate thrusts. First, to obtain international acceptance of a thermodynamically-based, metrologically sound protocol for pH measurements; and second, to assess the degree of agreement which is attained in interlaboratory measurements of primary pH standards at the highest metrological level.

Problem: Since 1985, the International Union of Pure and Applied Chemistry (IUPAC) has recommended two mutually inconsistent protocols for pH metrology. The first is the "multi-point" protocol originally developed at NIST (then the National Bureau of Standards) in the 1950s. This protocol is based on thermodynamic theory and assigns standard pH [pH(PS)] values to a set of consistent standard buffers based on measurements in electrochemical cells with no liquid junction. The second protocol relies on non-thermodynamically based measurements to assign (with significant subsumed errors) pH values of a set of operational buffers [pH(OS) standards]. Values measured for identical standard buffers by the two protocols [pH(PS) and pH(OS)] can differ by as much as 0.02 pH unit. This lack of comparability is unacceptable. Quantitative information on horizontal traceability at the highest metrological level [the pH(PS) standards] is essential to international acceptance of the NIST protocol for pH metrology.

Approach: Led by NIST, the national metrological institutes (NMIs) in 1997 voiced strong objections to the IUPAC dual protocol. As a result, IUPAC formed a pH Working Party (pH WP), that included members from NIST and other interested NMIs. The pH WP was charged with resolving the present dual protocol and generating a new recommended protocol reflecting present thinking on good metrological practice. NIST participated in the activities of the pH WP to ensure that any final protocol that was generated would be based on thermodynamic theory and would not adversely impact U.S. industry.

To establish international horizontal traceability at the highest metrological level, NIST participated in an international comparison organized by EUROMET (an association of EUROMET NMIs) to provide an inter-regional link in this study. This enabled benchmarking of NIST activities in pH(PS) value assignment against the parallel efforts of four other participating NMIs. In this comparison exercise, values of pH(PS) were assigned by each of five participating NMIs using the NIST protocol for borate and carbonate.

Results/Future Plans: The NIST multi-point pH protocol has achieved prominence in the newly proposed IUPAC recommendations for pH metrology. The revised IUPAC protocol for pH, currently under development, incorporates the metrological principles of traceability, primary and secondary measurements, and treatment of uncertainties. In essence, it recognizes the multi-point protocol as the basis for pH metrology and eliminates the concept of pH(OS) standards. It specifically relegates all standards not measured via the multi-point protocol to a secondary status. NIST participation in the pH WP has been crucial in the attainment of a single, metrologically acceptable protocol. Future participation is essential to ensure that the final IUPAC document remains in accordance with these agreed goals and represents good metrological practice.

The results obtained by the five participating NMIs in the international pH(PS) comparison indicate that the assignment of pH(PS) for these buffers is precise to less than ±0.005 pH units, similar to values estimated by the other participants. These results confirm that NIST is at or above the state-of-the-art in primary pH metrology. Future, similar comparisons are essential to provide ongoing verification of international horizontal traceability, and ideally, to improve inter-NMI agreement on pH(PS) values.

25. Developing Gas Mixture SRMs through International Collaborations with Selected Partners

F.R. Guenther

Objective: To increase the production and certification of NIST traceable gas standards such that end users requiring NIST traceability will always have a source for the needed standard(s).

Problem: NIST traceable gas standards are in high demand worldwide as a source of traceability to the mole. Many countries require traceability to NIST to meet regulatory goals, or need NIST traceable gas standards to satisfy import requirement of goods into the U.S.. In addition, U.S. companies frequently require NIST traceable gas standards in order to do business in the international arena. Thus it is imperative that NIST improve and extend the production of NIST traceable gas standards to meet these demands.

Although gas NIST Traceable Reference Materials (NTRMs) are now available through specialty gas producers, they have not proven to be a direct replacement for gas SRMs in all cases. Regulations, especially in the automotive industry, specifically require the use of SRMs due to the tight tolerances required on the uncertainty of the certified value. In addition, NTRMs are not generally available for sale to end-users because the producers prefer to use them in the production of EPA protocol gas standards, a highly lucrative market. Thus there is still a need for gas SRMs and this need will not disappear in the foreseeable future. NIST alone does not have the resources to maintain all gas SRMs in-stock at all times and thus an alternative approach must be found.

Approach: For the past five years, NIST has worked with the Netherlands Measurement Institute (NMi) to establish equivalence in gas standards between the U.S. and Europe. This program has been very successful; the EPA now recognizes the Equivalence Agreement in its regulations and, therefore, specialty gas producers can use NMi standards when preparing EPA protocol gas standards. By building on that relationship, NMi becomes the natural selection for a second source of NIST gas SRMs. In the immediate future, when a gas SRM becomes out-of-stock, NIST can purchase gas standards from NMi for immediate sale as gas SRMs. Since the present equivalence agreement demonstrates comparability to ± 0.5 %, NIST would only have to quality assure the standards against our primary standards before they could be sold as SRMs. This process should require minimal effort and thus save considerable time.

As a third source of NIST gas SRMs, plans are in place to develop a relationship with an Asian national metrology laboratory. NIST has not yet identified a suitable partner in Asia; however, we anticipate we would develop an Equivalence Agreement with the identified laboratory as was done with NMi.

Future Plans: As the relationships with our international partners mature, we plan to extend the agreements from their being just a source for candidate gas SRMs, to being a full partner in the production and certification of NIST traceable gas standards. This can be accomplished in several ways, from a direct source of NIST SRMs, to a certifying agent for NTRMs. These issues will be discussed over the next year and a plan established to phase in this program. In addition, the equivalence agreement with NMi will be refocused in light of this program to achieve agreement to within 0.25 % for most analytes.

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