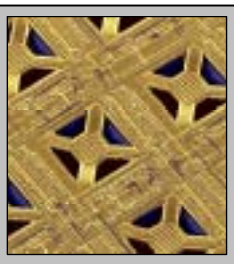
# Process Measurements Division - Table of Contents


| | |
|---|---|
| Division Overview | 2 |
| Thermophysical Properties of Gases used in Semiconductor Processing | 17 |
| Atomic Standard of Pressure | 20 |
| Development of High-Precision Isotope Reference Standards | 22 |
| International Comparisons of Pressure Standards | 24 |
| Measurements for Vacuum Process Control | 27 |
| Improved Vacuum Transfer Standards | 28 |
| Transducer-Assisted Piston Gauge Calibrations | 30 |
| Electronic Structure and Transport in Model Molecular Electronic Systems | 32 |
| DNA and protein gel plugs for biological assays | 34 |
| Temperature Gradient Focusing | 36 |
| Development of Process Monitoring and Diagnostic Techniques | 38 |
| Chemical Analysis Through Rapid Micro-Boiling Events | 40 |
| Carbon Nanotubes (CNTs) on Microhotplates | 42 |
| Efficient Development of Materials for Chemical Sensing Using MEMS-Based Microarrays | 44 |
| Chemical Warfare Agent Detection with Microsensor Arrays | 46 |
| Error Free Liquid Flow Diverters for Calibration Facilities | 48 |
| Non-Contact Free Carrier Density Measurements for Compound Semiconductors | 50 |
| Benchmark Data on Liquid Fire Suppressants | 52 |
| Standards for Raman Spectroscopy | 54 |

# Process Measurements Division

**James R. Whetstone, Chief**
**George E. Mattingly, Deputy Chief**



- Process Measurements

***J. Whetstone, Chief***

- **Fluid Flow**
- **Process Sensing**
- **Thermometry**
- **Pressure & Vacuum**
- **Thermal & Reactive Processes**
- **Fluid Science**

## Division Overview

***Mission:***

The Process Measurements Division establishes and disseminates national measurement standards for thermodynamic parameters and engages in measurement science research to improve measurement capabilities for chemical process and related technologies. Research efforts enhance U.S. national measurement standards, their realization and dissemination, measurement techniques, recommended practices, sensing technology, instrumentation, and mathematical models required for analysis, control, and optimization of industrial processes. The Division is responsible for national measurement standards for temperature, humidity, pressure and vacuum, fluid flow, air speed, liquid density and volume. Its research efforts seek fundamental understanding of, and generate key data pertinent to, chemical process technologies. 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, physical property, and engineering data.

**Organizational and Project Structure:**

The Division has 69 full-time staff members, organized in 6 groups, representing a range of technical competencies and is organized to establish, strengthen and extend them. Competencies, research efforts, and standards activities are focused in the 12 project areas shown at the right. The 2-digit Process Measurements Division group number or the 3-digit NIST Division number given in square brackets in the project listing indicates group or Division responsibilities for each project. In several cases competencies required for successful accomplishment of project objectives cross Group and/or Division organizational lines.

***Process Measurements Division Projects***

- Flow Measurements and Standards [01, 06]
- Temperature Measurements and Standards [05, 08]
- Pressure and Vacuum Measurements and Standards [06]
- Humidity Measurements and Standards [05]
- Microfluidics and BioMEMS [04, 839]
- Chemical Sensing with Micro-Arrays [04]
- Molecular Electronics [00, 837, 812]
- Plasma Process Metrology [04]
- Advanced IC Interconnects – Process Metrology and Models [07]
- Optoelectronics [07, 837, 839]
- Acoustic Measurements and Methods for Thermophysical Properties [08]
- Particulate Standards and Measurements [07, 837]

## Competencies and Accomplishments

The following describes the Division's group organization, competencies, and project responsibilities. These are followed by descriptions of project accomplishments in the context of CSTL programs.

### *Fluid Flow Group – 836.01*

- Flow rate measurements;
- Computational fluid dynamics;
- High accuracy liquid volume and density measurements and standards; and
- Anemometry.

Primary responsibility for the Flow Measurements and Standards project.

***Process Sensing Group – 836.04***

- Plasma processes, models, radio frequency and optical diagnostic and measurement methods;
- MEMS-based gas sensor arrays, deposition of gas sensitive thin films, and operation and testing of gas sensors;
- Mono-molecular self-assembly chemistries;
- DNA probe/target sensing approaches; and
- Molecular recognition strategies.
- Physical and chemical measurements in micro-fluidic devices.

Primary responsibilities for the Plasma Process Metrology, Chemical Sensing with Micro-Arrays, and Micro-Fluidics and Bio-MEMS projects.

***Thermometry Group – 836.05***

- Development and operation of fixed-point cells defining temperature scales;
- Primary acoustic thermometry;
- Resistance thermometry;
- Cryogenics and low temperature thermometry;
- Thermodynamic methods for the generation of moisture in gases – humidity measurements; and
- Cavity ring-down spectroscopy - gas and liquid.

Primary responsibilities for the Temperature and Humidity Measurements and Standards projects.

***Pressure and Vacuum Group - 836.06***

- Primary manometry;
- All aspects of vacuum gauging;
- Very low gas flow rate measurements and standards;
- Piston gauge characterization and calibration; and
- Pressure gauging of all types.

Primary responsibility for the Pressure and Vacuum Measurements and Standards project.

***Thermal and Reactive Processes Group – 836.07***

- Raman Spectroscopy;
- Optical diagnostic techniques;
- Aerosol transport and diagnostic measurements;
- Computational fluid dynamics;
- Chemical vapor deposition reactor modeling;
- Combustion processes; and
- Liquid atomization.

Primary responsibilities for the Advanced IC Interconnects – Process Metrology and Models, Optoelectronics, and Particulate Standards and Measurements projects.

***Fluid Science Group – 836.08***

- Measurements of thermophysical and properties of fluids and fluid mixtures;
- Statistical Physics;
- Equations of State;
- Acoustic measurement techniques; and
- High accuracy capacitance measurements;

Primary responsibility for the Acoustic Measurements and Methods for the Thermophysical Properties project. Contributes to the Pressure and Vacuum, Temperature and Flow Rate Measurements and Standards projects.

---

**Project and Program Areas:**

The Division's measurement science research and and standards realization and dissemination activities generate accomplishments in several of the 14 CSTL program areas shown at the right. The Division has responsibilities for establishing, enhancing, and disseminating national measurement standards, summarized in the first four project descriptions given below. A general competency in calibration metrology is a strong contributor to meeting these responsibilities. We provide traceability of measuring instruments for U.S. industry and government agencies primarily by provision of instrument calibration services and special tests. Where traceability of measurements is

***CSTL Programs***

- Automotive and Aerospace
- Biomaterials
- Pharmaceuticals and Bio-Manufacturing
- Chemical and Allies Products
- Data and Informatics
- Energy Systems
- Environmental Technologies and Services
- Food and Nutritional Products
- Forensics and Homeland Security
- Health and Medical Products and Services
- Industrial and Analytical Instruments and Services
- Microelectronics
- International Measurement Standards
- Technologies for Future Measurements and Standards

more effectively provided to customers through Standard Reference Materials and Data, we utilize those mechanisms. We demonstrate the level of equivalence of U.S. national

measurement standards with those of other nations by participating in comparison efforts organized by the Comité International des Poid et Mesures (CIPM), by the CIPM's consultative committees and by Regional Metrology Organizations. NIST is a leading member of the Sistema Interamericano Metrologia (SIM – the Inter-American Metrology System). These efforts occur in several Groups and support CSTL's International Measurement Standards program.

***Temperature Measurements and Standards***

NIST was the first NMI to fully realize the ITS-90 for contact thermometry in the range of 0.65 K to 1235 K. The Process Measurements Division effectively disseminates the ITS-90 to a broad range of users. Research efforts focus on advancing the state-of-the-art in thermometry by developing methods and devices that enable industrial users to attain traceability to the ITS-90 in demanding industrial environments. Furthermore, this project:

- Assists user groups in the assessment and enhancement of the accuracy of their temperature measurements,
- Promotes effective measurement methods through participation in standards development organizations,
- Measures the deviations of the ITS-90 from thermodynamic temperature values as a basis for future improvement of temperature scales, and
- Improve temperature measurements and standards

***Flow Measurement and Standards***

National measurement standards for fluid flow rate and related quantities are developed and disseminated through the following calibration services:

- Gas flow rate – 0.04 to 77,600 slm;
- Water flow rate – 8 to 38,140 slm;
- Liquid hydrocarbon flow rate – 0.04 to 1,140 slm;
- Liquid volume – 3.8 to 7,600 L;
- Liquid density – 600 - 2000 kg/m$^3$;
- air speed in the range of 0.2 to 75 m/s.

Research efforts advance the state-of-the-art in flow measurements through the development of measurement standards that minimize measurement uncertainty and improve the quality of fluid measurements for the custody transfer of fluids in commerce. The Group's efforts establish levels of comparability among National Metrology Institutes (NMIs) and strengthen measurement traceability procedures of U.S. national standards for flow rate measurement.

***Humidity Measurements and Standards***

National measurement standards for humidity are developed to extend their range and reduce measurement uncertainty and are disseminated through calibration services. Research efforts and standards activities focus on:

- Providing access to national measurement standards through the provision of measurement services available to industry, government, and the public;
- Developing and enhancing primary humidity measurement standards;
- Demonstrating levels of equivalence of U.S. national measurement standards with those of other nations; and
- Engaging in education and outreach efforts to improve industrial hygrometry practices.

Water vapor is a primary contaminant in process gases required by many industrial processes. Integrated circuit manufacturing requires very low moisture (μg/g and ng/g) levels. The Division is disseminating through instrument calibration services and special tests. We are developing rapid, low cost methods for calibration of permeation tube generators to provide semiconductor manufacturers, gas suppliers, and instrument makers with standards of improved accuracy to facilitate improvements in process control.

***Pressure and Vacuum Measurements and Standards***

Pressure and vacuum measurements are used in industrial, aerospace, and transportation applications to achieve manufacturing quality, throughput, and performance. In many cases pressure and vacuum measurements are important to public health and safety. The efforts of this project:

- Provides national measurement standards for pressure and vacuum, (from $10^{-7}$ to $10^{+8}$ Pa) and low gas flowrate ($10^{-13}$ to $10^{-3}$ mol/s) through the provision of measurement services available to industry, government, and the public;

- Develops improved measurement standards and techniques for pressure, vacuum, and low range flow measurement;
- Demonstrates levels of equivalence of U.S. national measurement standards with those of other nations.

Research activities improve the realization of both primary and transfer standards to anticipate future measurement and standards needs of industry. Research efforts improve efficiency and accuracy of calibration services, both those supplied by NIST and by NIST's customers. Examples of current research efforts include projects to develop:

- An intrinsic primary pressure standard based on the dielectric constant of helium calculated from first principles;
- Next-generation vacuum gauging technology to unstable ionization gauges;
- Improved low-range flow rate standards; and
- A database of out-gassing rates from stainless steels to enable construction of chambers to achieve extreme vacuum levels.

***Chemical Sensing with Micro-Arrays***

Real-time sensing of gas phase chemical species has application areas as diverse as automotive exhaust gas speciation to detection of chemical warfare agents. Chemical micro-sensor arrays are based on NIST-developed, and patented, 'micro-hotplate' (μHP) arrays formed by silicon micro-machining and similar devices such as differential-scanning calorimeters. 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 capable of detecting a range of organic species. Both species identification and quantification have been demonstrated with individual devices and arrays. Methods have been developed and demonstrated that significantly increase the sensitivity and stability of micro-hotplate chemical sensors. Sensitivity to organic analytes, e.g., methanol in air at the 10 ng/g level, has been demonstrated as has sensitivity to similar levels of chemical warfare agents. Nanophase, doped sensing oxides have been shown to produce high sensitivities without the fouling effects that are often observed on metal catalyst-doped films.

***Micro-Fluidics and Bio-MEMS***

Micro-fluidic and Bio-MEMS device technologies promise to accelerate the merging of biological systems with micro-machined technology to develop selective, miniaturized chemical and biochemical measurement tools incorporating molecular recognition and related technologies. Research efforts seek to develop metrology methods and tools to characterize the performance of micro-fluidic devices and structures. These new tools hold tremendous promise for point-of-care health care measurements and for rapid detection of potential bio-terrorism pathogens. Major scientific and technical challenges to be overcome include:

- Developing robust, self-assembly-based protocols, with sub-micrometer resolution, for directing and attaching biological molecules to MEMS structures;
- Developing analytical techniques for characterizing the activity of biological/MEMS structures;
- Ensuring compatibility of MEMS devices with aqueous biological environments; and
- Developing novel MEMS-based transduction strategies for detecting biological recognition events.

Current research is focused on a model, prototypical BioMEMS device and reaction: the melting of DNA on μHP devices. The heat producing and temperature measurement capabilities of μHPs hold great promise for monitoring and detecting biological reactions in MEMS device formats.

***Advanced IC Interconnects – Process Metrology and Models***

To achieve higher operating frequencies, semiconductor devices of the future will be fabricated with on-chip interconnections (wiring) consisting of thin films having dielectric constant values lower than that of currently used silicon dioxide. In addition, copper will replace aluminum as the interconnection metal. Low dielectric constant (Lo K) films are composed of a number of materials systems most of which are porous.

Copper readily diffuses through the currently used $SiO_2$ films necessitating the use of thin diffusion barrier layers placed between the copper bulk conductor and the dielectric, $SiO_2$. Use of Lo K insulating films will also require diffusion barrier layers effective on surfaces of varying porosities and with thickness of 10 nm and below for feature sizes in the sub-100 nm region. A variety of metrology needs are associated with the use of Lo K materials at sub-100 nm features dimensions. Although recent advances in the electrochemical deposition processes currently used for copper deposition are anticipated to meet deposition needs below 100 nm feature sizes, these require a seed layer to operate effectively. The currently used physical vapor deposition of seed layers is not useful for sub-100 nm where aspect ratios of 10:1 are planned. Chemical vapor deposition of copper is the process that has been identified as the best candidate for seed layer deposition. The International Technology Roadmap for Semiconductors – 2000 Update has a "No Known Solution" entry for many of the process modeling and simulation requirements necessary to support development and copper CVD for interconnect seed layers and fills is identified as an area requiring research. Research efforts address the need for the development of fundamental reaction mechanisms and rate constants (both gas/plasma and surface) that are key to properly capturing the physics and chemistry of surface evolution during thin film deposition. Research efforts seek to:

- Develop models of thermal decomposition models for deposition of both diffusion barrier and metal layers in Lo-k materials;
- Develop and validate 1 and 2 dimensional reactor models that include particle formation, agglomeration, transport, fluid dynamic and thermophoretic effects;
- Develop process metrologies supporting deposition of copper seed layers; and
- Investigate atomic layer deposition methods as an alternative to chemical vapor deposition for ultra-thin barrier layers.

***Optoelectronics***

Free carrier transport is central to the operation of all optoelectronic devices. Measurement of free carrier concentration and mobility is critical in determining the material quality. Current practice utilizes Hall Effect or capacitance probe methods that require electrical contact to metal probes. If available, non-contacting methods would allow in-situ and ex-situ measurement and inspection. A spatially resolved method would also provide the means improve process uniformity and control. Raman spectroscopic methods do not require physical contact with the material in addition to having excellent sensitivity to interaction between free carriers and polar lattice vibrations. From the Raman spectrum, the majority carrier properties are determined by fitting of appropriate spectral models. Research efforts seek to:

- Develop in situ, non-destructive probes of III-V semiconductor carrier properties suitable for spatially resolved measurement and process monitoring and control during film growth and etch processing;
- Incorporate temperature dependence on materials properties, i.e., band structure, carrier concentration, and carrier effective mass to allow measurements at growth temperatures; and
- Develop a spectral simulation model for quantitative determination of carrier concentration and mobility from Raman spectra.

***Plasma Process Metrology***

Some of the most important processes in semiconductor manufacturing are plasma processes used to deposit and etch the thin films that form integrated circuit devices. Plasma processing reactors have historically been designed and operated using empirical methods alone, but continued evolution of these manufacturing tools requires a much greater reliance on process and reactor modeling. Indeed, model-based process design and control are important needs 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. Experimental

efforts use reference reactors as test beds for validating models and testing new measurement techniques. These reactors provide a well-defined basis for comparison of measurements between laboratories and are equipped with a wide variety of plasma diagnostic tools that measure the chemical, physical, and electrical properties of plasmas. Information provided by the set of diagnostics allows testing of models. Also, sensors designed for manufacturing environments can be tested and compared with diagnostic results. These efforts are combined with complementary tasks undertaken by EEEL and PL.

Research efforts seek to:

- Develop advanced chemical and electrical measurement methods, diagnostic techniques, and models to characterize plasma etching and deposition processes to enhance continued progress in process optimization, process control, and model-based reactor design;
- Develop rf electrical measurement techniques for the accurate determination of electrical parameters in rf plasma reactors supporting comparison of reactor performance and operating conditions and set points; and
- Develop plasma sheath models for use with rf electrical measurements to non-intrusively determine ion flux and energies at the wafer surface. Utilize these developments as the basis for new approaches to non-invasive measurement of plasma parameters.

***Molecular Electronics***

As silicon-based electronics components approach inherent performance limits, small molecular ensembles are seen as the active elements are seen as a viable, next-generation technology. NIST is developing measurement methods, standards, and data that are critical to the realization of molecular electronic components. This project is collaborative with Divisions 837, 838, and EEEL.

Research efforts seek to develop:

- Test structures supporting characterization of the electrical properties of ensembles of molecules;
- Methods and procedures to evaluate current-voltage transport in molecular systems;
- Models of electronic structure/transport mechanisms in molecular electronic systems; and
- Computational models of conducting molecules.

***Acoustic Measurements and Methods for Thermophysical Properties of Gases***

The thermophysical and transport properties of gases are important in a broad range of industrial processes ranging from thermo-acoustic machine design to flow rate measurement. The Division investigates fundamental physical acoustics and develops versatile and rugged acoustic resonator methods to produce accurate measurements of the speed-of-sound and viscosity of gases.

A modified Greenspan acoustic resonator with specialized transducers is being developed to measure the bulk viscosity of xenon near its critical point in earth's gravity and, eventually, in micro-gravity. These measurements will be made closer to the critical point than ever before and may resolve long-standing discrepancies between theory and experiment. This work exploits expertise gained from the previous measurements of the shear viscosity of near-critical xenon in micro-gravity.

Mass flow controllers (MFCs) are ubiquitous for gas delivery to process chambers used in integrated circuit manufacturing. Individual process tools use 20 - 50 MFCs often operating in the flow rate range 1 to 1000 sccm. Continued increases in process reproducibility requirements drive improvements in MFC accuracy and stability. Thermophysical property data are used to calculate gas conversion factors that predict MFC flow performance with reactive process gases from calibration data obtained with non-reactive gases. NIST research will improve standards in this low flow rate range and thermophysical property data for chemically reactive process gases with efforts to:

- Measure the equation of state and transport properties of the gases used in semiconductor processing with the uncertainties required by industry;
- Develop computational tools for evaluating, correlating, and (where possible) predicting these properties, and
- Disseminate property data via a user-friendly database and archival publications. As data are acquired, they are posted at http://properties.nist.gov/fluidsci/semiprop/. The properties are : speed-of-sound, heat capacity,

density (equation of state), viscosity, and thermal conductivity.

***Particulate Measurements and Standards***

A major coordinated effort across Federal and State agencies is underway to improve the understanding of airborne particulate matter (PM) and its effects upon human health. An essential element in advancing the atmospheric science of fine particles is the ability to make reliable measurements of the physical and chemical properties of the particulate matter. Significant uncertainty exists regarding the quality of the measurements, and how well the data sets represent the actual PM source signatures. Several NIST Divisions will develop metrologies and PM reference materials for calibrating analytical instrumentation that discriminate and quantify PM-carbon into elemental, organic, and inorganic fractions. Three types of materials are necessary to allow measurement traceability to standards and improve inter-laboratory reproducibility.

- pedigree PM (i.e., non-complex PM with clear traceability to the SI),
- simulated PM (i.e., blended mixtures of non-complex PM materials to resemble real PM), and
- real PM (serving as measurement benchmarks).

PM reference materials supplied by industry cannot be traced to the SI. Thus NIST cannot assign certified values. The capability to manufacture reproducible carbon particles in sufficient quantities to serve as a standard reference material is needed. The NIST reference spray combustion (NRSC) facility is such a unique, highly controlled, and characterized benchmark industrial-like facility, which can serve in this capacity. Because this experimental facility can reproduce a range of combustion conditions similar to a variety of industrial sources and is well diagnosed, its use to generate PM provides the opportunity to correlate well characterized combustion conditions and chemistries with PM which will also be well characterized. The measurement issue addressed is reproducible control of the chemistry in this facility so as to generate the particulate composition and purity with quantitative uncertainties.

Research efforts seek to develop:

- A suite of reproducible carbon-based PM reference materials with properties closely approximating that of natural PM;
- A benchmark data set that correlates liquid-phase fuels and combustion characteristics (droplet/particle characteristics/dynamics, chemistry) with that of the PM material (morphology, thermo-optical properties); and
- Provide data for droplet-laden, homogeneous turbulent flow around obstacles for validation of fire suppression models.

**Division Contributions to CSTL Programs:**

The Division research efforts and standards activities contribute to the following CSTL programs:

- Automotive and Aerospace
- Data and Informatics
- Energy Systems
- Forensics and Homeland Security
- Health and Medical Products and Services
- Industrial and Analytical Instruments and Services
- International Measurements and Standards
- Microelectronics
- Technologies for Future Measurements and Standards

Brief descriptions and summaries of some FY 2002 accomplishments follow. More detailed descriptions of these accomplishments are given in the 20 technical articles that follow this overview.

***Industrial and Analytical Instruments and Services Program***

The instrumentation manufacturing industry is an important customer for NIST, providing a broad interface between NIST standards activities and end users of measurements. The Division disseminates U.S. national measurements standards and develops improved methods of realization of national measurement standards. Most of these efforts occur in the four standards-oriented projects of the Division: Fluid Flow, Temperature,

Pressure and Vacuum, and Humidity. Division Staff interact with a wide variety of instrumentation manufacturers who rely on our measurement services to provide traceability to U.S. national measurement standards.

Calibration Services

Although Standard Reference Materials (SRMs) and Data (SRDs) are utilized in some cases to disseminate measurements standards, instrument calibration services are the primary method used by the Division for dissemination purposes. The chart in Figure 1 summarizes the level of activity in the major calibration service areas offered over the period 1998 thru 2002. Substantial yearly fluctuations in calibration requests are often encountered. The total workload for calibration shows a small decrease in this period.

Quality System Supporting Calibrations

A policy for a NIST-wide quality system to support calibration services will be established in FY03. Efforts in the Process Measurements Division to establish a quality system have moved forward substantially in FY02 through the completion of the initial phase of quality system documentation. An initial internal assessment/audit based on ISO 17025 began late in FY02 and will be completed in early FY03 using NIST staff drawn from both the Process Measurements Division and other NIST Divisions for this assessment. These efforts support NIST's self-declaration of its quality systems supporting it Calibration and Measurement Certificates in compliance with the CIPM Mutual Recognition Arrangement.

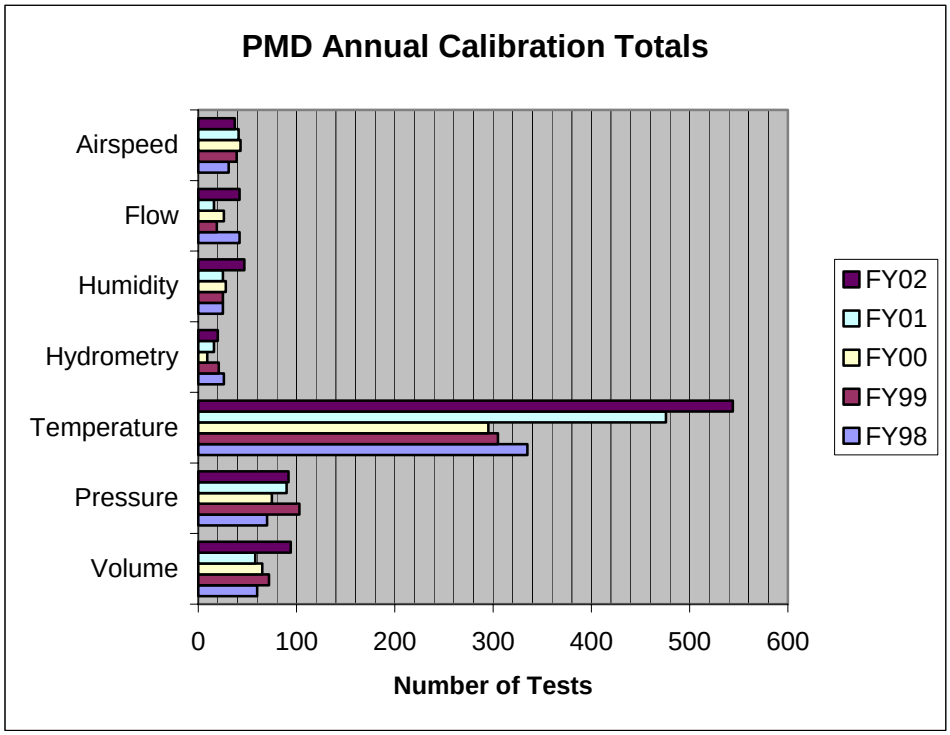
Improving the Realization of Measurement Standards

Research efforts associated with our standards activities seek to improve realizations of our national primary standards that are the basis for providing measurement services to our customers. A number of accomplishments in FY02 are having significant impact on the ability of the Division to disseminate these standards and on their uncertainty.

In the Fluid Flow Project, an effort to significantly reduce the measurement uncertainty for low to moderate range gas flow rate standards has resulted in development of a new primary gas flow standard based on the pressure, volume, temperature, and time (*PVTt*) method that has an expanded uncertainty of 0.02% to 0.05%. This is a 5-fold improvement over our previous capabilities. We believe that the NIST gas flow calibration service is the "best in the world". Additional improvements are anticipated that will decrease the uncertainty by an additional factor of 2. Refurbishment of the water flow rate measurement facility is scheduled for completion in mid-FY03. Research on methods to reduce this gravimetrically based system's measurement uncertainty have resulted in development to substantially reduce diverter valve effects on the uncertainty. Several variations in the general approach have been developed conceptually and one was chosen for testing and implementation. Initial testing indicates substantial reduction in diverter error component contribution. This design has been incorporated into the refurbished facility. The development of intrinsic pressure standards in the range 0.3 MPa to 5 MPa is a long-term Division goal that is based on both the measurement and first principles calculation of the dielectric constant $\varepsilon(p,T)$ of helium. The extraordinary accuracy of quantum mechanics-based calculations continue to improve. This new approach to primary standards for pressure will permit the determination of the pressure $p(\varepsilon,T)$ from electrical and temperature measurements to have a smaller uncertainty than the determination of pressure using existing methods to realize standards (piston gages), which are thought to be reaching the practical limits of their realization.

A transducer-assisted piston calibration technique has been demonstrated that from 20 to 200 MPa on a hydraulic system. The resultant uncertainties compare very favorably with the prevailing fall-rate method. This method improves piston gauge calibrations by reducing or removing operator judgment and manual data entry, and introduces more consistency through automation, with no penalty in overall uncertainty. Extension of this approach to pneumatic gauges will be pursued in FY03. The method substantially reduces the

time necessary to complete calibration procedures with no reduction in measurement uncertainty.




**Process Measurements Division Instrument Calibrations for Fiscal Years 1998 through 2002**

***International Measurement Standards***

NIST is the U.S. National Metrology Institute (NMI) and the agency of the U.S. Government responsible for U.S. efforts under the Treaty of the Metre. The Committee International des Poids et Mesures (CIPM), and its various consultative committees, organizes comparison of national meaurement standards. In addition, coordination of similar efforts with Regional Metrology Organization (RMO) such as the Sistema Interamericano Metrologia (SIM), which includes the countries in the Americas, extend the comparison efforts to as many participants as practicable.

In October 1999, NIST signed the CIPM Mutual Recognition Arrangement (MRA). The objectives of the MRA are:

- To establish the degree of equivalence of national measurement standards maintained by NMIs;
- To provide for the mutual recognition of calibration and measurement certificates (CMCs) issued by NMIs; and
- Thereby to provide governments and other parties with a secure technical foundation for the wider agreements related to international trade, commerce and regulatory affairs.

Since 1999 the Division systematically compared U.S. national measurement standards to establish degrees of equivalence of U.S. national measurement standard with those of other NMIs. Additionally, CMC capabilities reflecting our calibration services have been placed in the BIPM database developed for their publication. These international activities add value to NIST calibration services, particularly for our customers involved in international trade. These MRA-related activities guarantee recognition of U.S. standards by U.S. trading partners.

NMIs signatory to the MRA are required to use a quality management system to ensure the continued validity of the claims of calibration and measurement certificates remain valid. Division efforts to develop such a system were described above.

The Process Measurements Division has significant participation in the CC's for Temperature (CCT) and Mass (CCM). We have lead or participated in many KCs in the past several years. In thermometry, these efforts have resulted in establishing equivalence levels over the ITS-90 range from 14 K to 1235 K. KCs organized by the CCM include Division activities in both the pressure and vacuum and the flow project areas. In the pressure and vacuum project the Division leads or participates in KCs that cover the pressure range $3x10^{-6}$ Pa to 500 MPa. NIST has piloted three CCM Key Comparisons in the last several years, completing two in FY02 that demonstrated general equivalence among the participants, revealed no systematic bias between alternative realizations of the Pascal, were the only CCM KCs completed on schedule, and set the standard for the manner in which KCs should be conducted. A summary of these activities and accomplishments is given in the technical reports following this overview.

G. E. Mattingly of NIST chairs the CCM's Working Group for Fluid Flow (WGFF). The WGFF has formed its strategy, structure, and schedule for comparisons in six areas: water, hydrocarbon liquids, low-pressure air, and high-pressure, high-flow natural gas, air speed, and liquid volume. The WGFF chair, working closely with the NIST Statistical Engineering Division, has developed a sound, statistically based experimental design and supporting analysis method applicable to all KCs. The design of these protocols and transfer standards will set precedents that should advance the state-of-the-art in conducting all future flow laboratory comparisons. This metrological plan was presented to the CCM in May 2002. The BIPM Director noted that this plan should result in a unique comparability of the flow standards in the participating NMIs and to fulfill "the Ideal of the MRA".

In each area, a task group has been formed where one NMI, termed the Initiating Laboratory, has accepted responsibility to select fluids and flow conditions for the KC and to develop and assess the performance of a transfer standard in the conditions selected for the comparison, thereby

quantifying its baseline metrological performance level. Two additional NMIs, representing different RMOs, termed assisting labs, will conduct tests on the transfer standard to independently quantify performance levels. Once acceptable, quantifiable performance levels are achieved, 2 additional transfer packages are assembled and tested by the initiating and assisting laboratories. The initiating and assisting laboratories then arrange and monitor the tests in each RMOs so that the requisite data is produced in timely manner.

NIST will pilot the KC for the low-pressure gas flow. Recent advances in U.S. standards and procedures (see accompanying technical report) are expected to materially improve the performance-level of this KC. Characterization of the transfer package will begin in FY03.

***Microelectronics***

The NIST National Semiconductor Metrology Program (NSMP) is managed by the Office of Microelectronic Programs (OMP) of the NIST Electronics and Electrical Engineering Laboratory. CSTL competencies in several areas contribute to metrology developments needed in semiconductor manufacturing. Working with the OMP, the Division selects, develops, evaluates, and validates process measurement technologies important in semiconductor manufacturing. Several projects support advances in semiconductor metrology focused on specific manufacturing technologies where metrology issues must be resolved to realize goals set by the industry. Division efforts include:

- Development of measurement techniques and expertise supporting the evolution of molecular electronic device architectures;
- Development of thermocouple technology for control of thermal processing equipment, including thin film/wire instrumented silicon wafer technology to support in-situ calibration of radiometric devices used for control of rapid thermal processing (RTP) systems;
- Improved standards and data for mass flow controllers include improvement in low-range gas flow standards and provision of transport property data for chemically reactive process gases;
- Develop quantitative measurement capability to enable a real-time, *in-situ* semiconductor process-control based on optical diagnostic and improved flow calibration techniques;
- Measurements and models supporting advanced interconnect processes based on low dielectric constant thin films and future generation metalization strategies;
- Methods to determine electrical, physical, and chemical properties of plasmas used for etching and reaction chamber cleaning processes; and
- Water vapor measurements and standards below the μg/g level for contamination control in process gases.

In some of these efforts, we make use of processing reactors 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, in the case of plasma reactors, complex electrical interactions, 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) ITRS. In fact, modeling is specifically identified not only as a "crosscutting technology," but also as "pervading all crosscuts." Our program in this area, partially supported by NIST's National Semiconductor Metrology Program, seeks to develop and validate benchmark chemical mechanisms and supporting thermochemical and kinetic data, for equipment and process design and control.

***Automotive and Aerospace***

Efforts in the Flow Measurements and Standards Project support the automotive industry and the EPA in the exhaust emissions metering area. Working with the American Industry-Government Emissions Research (AIGER) group, NIST designed a unique flow measurement facility to accurately meter synthesized automotive exhaust over normal operating ranges of IC engines. In

FY02 this facility was re-commissioned in anticipation of the need for characterization of metering devices to be used for monitoring of exhaust emissions necessary to demonstrate conformance with emission standards promulgated by the EPA. Testing is expected to commence in FY03.

***Data and Informatics***

Division efforts supporting this CSTL program result from activities in the Particulate Measurements and Standards projects where data involving the new generation of non-ozone-depleting Halon alternatives including chemical suppressants, are being developed to aid in the validation of CFD models being developed for fire suppression applications. An accurate representation of droplet transport is crucial to understanding the physics of droplet transport around and behind solid objects. Results have been obtained using particle image velocimetry, phase Doppler interferometry, and visualization techniques. A description of this work is given in the technical reports following this overview.

***Energy Systems***

Efforts in the Flow Measurements and Standards Project have the objective of demonstrating the level of equivalence of natural gas flow metering laboratories in North America. Custody transfer of natural gas utilizes metering stations in pipelines ranging in diameter from ~100 mm to ~1 meters. NIST is working closely with the Gas Technology Institute, the American Gas Association, and the Colorado Engineering Experiment Station, Inc. to develop testing protocols and a metering transfer standard to compare the performance of laboratories that calibrate the metering devices used in pipeline metering stations. Working with the NIST Statistical Engineering Division, we have developed the protocols and experimental design to be used. Testing began in late FY02. This work is scheduled for completion in FY03.

***Technologies for Future Measurement and Standards***

Research efforts in two Division projects primarily contribute to this CSTL program, the Chemical Sensing with Micro-Arrays and Micro-Fluidics and Bio-MEMS projects. The Chemical Sensor project is collaborative with the Semiconductor Electronics Division of the Electronics and Electrical Engineering Laboratory, and investigates advanced approaches to real-time sensing and measurement of gas phase chemical species based on solid-state chemical sensing arrays. Additionally, new methods and techniques are investigated supporting transduction strategies for measurement of gas phase, chemical species. Recent efforts have demonstrated for the first time the use of localized heating created by a micro-hotplate, a self-heating MEMS structure, in a cold CVD system to selectively deposit nanotubes on a microscale area. A combinatorial study was performed in which different elements of a 340-element array were exposed to different process conditions such as growth temperature and amount of metal catalyst. These efforts are described in more detail in the accompanying technical reports.

In the Micro-Fluidics and Bio-MEMS project research efforts have resulted in a number of accomplishments in FY02 addressing methods to concentrate and detect biological analytes in micro-fluidic systems. A new method for immobilizing biological capture-ligands in micro-fluidic devices has been devised with potential for application to disease diagnosis, and high throughput genomics and proteomics. Using photo-polymerization ligands, e.g., DNA or proteins, are covalently bound in a porous acrylamide gel plug formed in micro-fluidic channels. DNA or proteins that flow through the plugs can be captured and detected by an appropriate ligand. Use of multiple plugs, each containing a different biological ligand and spatially separated, are the basis for a multi-analyte detection strategy.

Temperature gradient focusing (TGF) is a new analyte concentration method invented in FY02 to meet the need for effective pre-concentration techniques in micro-fluidic device formats.

Initial experiments indicate that the new method has achieved greater than 10,000-fold concentration capability as well as utility for the focusing and separation of a variety of charged analytes including fluorescent dyes, amino acids, proteins, DNA, and colloidal particles. A patent application for TGF has been filed.

***Forensics and Homeland Security***

An application of the NIST-developed Chemical Sensing With Micro-Arrays project is the use of this approach to the detection of chemical warfare and related materials. Response testing of both simulants and agents have been conducted. Individual micro-sensors were tuned for specific agents by incorporating metal oxide films of different composition in arrays, and by selecting different fixed and time-varying temperature programs. Simulant material tests at NIST of appropriate device prototypes followed by testing at a surety laboratory investigating sensor array sensitivity, reproducibility, and stability are encouraging.

***Health and Medical Products and Services***

Extensive application of micro-fluidic devices to health related diagnostic products are anticipated. Incorporation of micro-scale detection will facilitate the use of these systems. A new electrical measurement method is being developed that is sensitive to the wetting properties of surfaces and the chemical composition of liquids. In this technique, thin film micro-heaters (μHs) immersed in a fluid are heated using a voltage pulse of 2-10 microseconds in length. Using the μH as a resistance thermometer, micro-boiling of the liquid, or bubble nucleation, is detected as a change in the heater temperature during the voltage pulse due to the difference in the thermal conductivity of the vapor versus that of the liquid. Complex micro-machined devices are not required; the measurement can be performed with structures as simple as a thin metal line on a substrate. The measurement is novel, easy to perform, and fast. The technique has potential for the detection of surface binding events such as those found in gene and protein chips.

***Awards in FY 2002:***

In FY02 several Division staff members received the following recognition and awards:

Aaron Johnson – Selected as a "Modern Day Technology Leader" for the 2002 Black Engineer of the Year Award Conference.

Gregory Strouse – DoC Bronze Medal in recognition of his exceptional leadership in the dissemination of temperature measurements and standards to U.S. industry and for establishing levels of comparability between U.S. national measurement standards and those of U.S. trading partners.

Archie Miiller – CSTL Technical Achievement Award in recognition of outstanding achievements for development of high stability and accuracy transfer standards that has enabled the effective comparison of primary pressure standards in the range 1 – 1000 pascals, resulting in two highly successful CIPM key comparisons.

Nancy Ortins Savage – Sigma Xi Outstanding Post-Doctoral Poster Award

Cary Presser – Elected as a Fellow of the American Society of Mechanical Engineering.

# Thermophysical Properties of Gases used in Semiconductor Processing

**CSTL Program:** Microelectronics
**Authors:** *J.J. Hurly, K.A. Gillis, and M.R. Moldover*

**Abstract:** CSTL is measuring the thermophysical properties of gases widely-used in semiconductor processing using novel, accurate, NIST-developed acoustic techniques. The properties include the speed-of-sound, ideal-gas heat-capacity, density (equation of state), viscosity, and thermal conductivity. The semiconductor industry has identified process gases, "surrogate" gases, "carrier" gases, and their binary mixtures that have the greatest need of accurate thermophysical property data. Accuracy targets for thermophysical property data have been established that meet the needs for modeling chemical vapor deposition (CVD) processes and calibration of mass flow controller (MFC) using surrogate gases. Measured data are disseminated as a database available via the internet at the URL http://properties.nist.gov/semiprop (Fig. 2) that includes the heat capacity at constant pressure, thermal conductivity, viscosity, and a pressure-density-temperature relation for process gases as well as the diffusion coefficients for the gaseous mixtures.

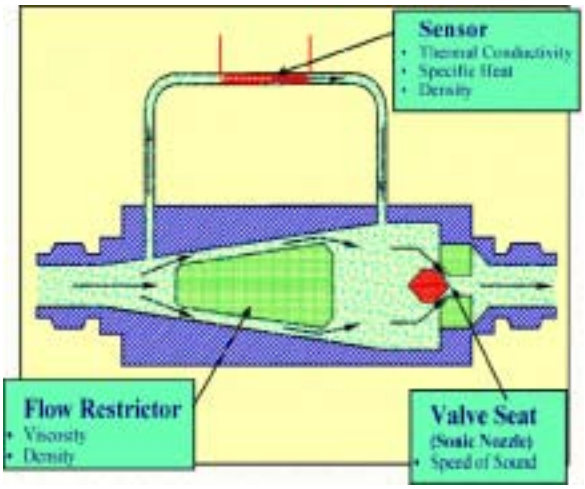
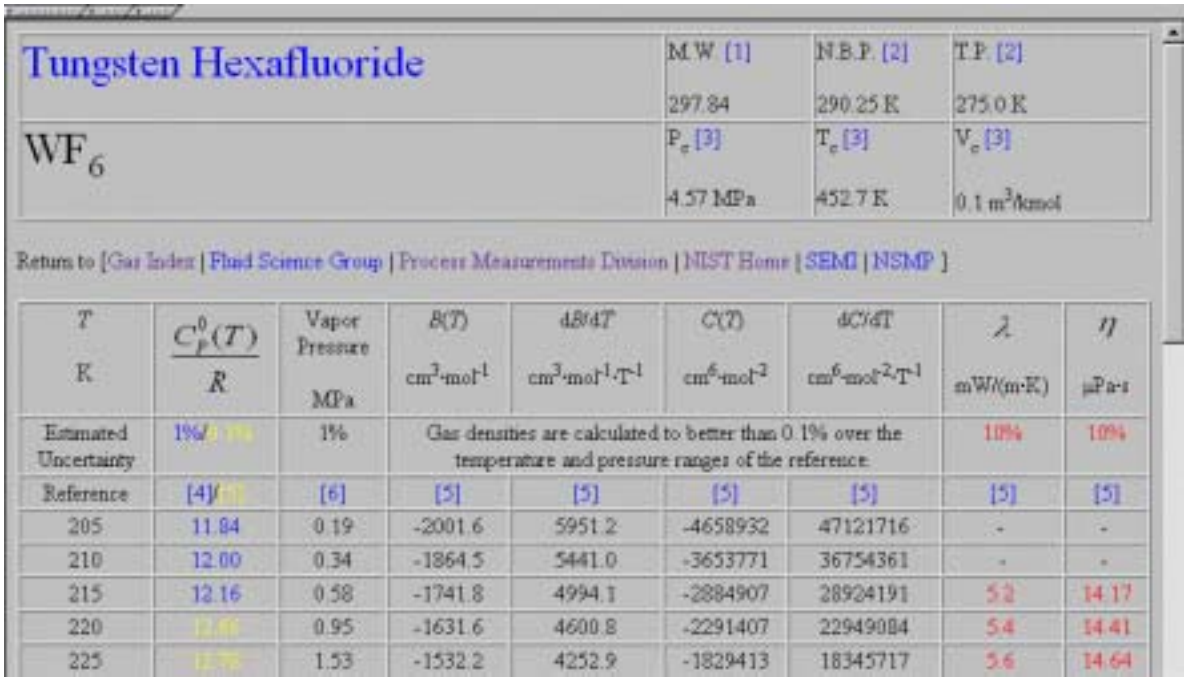



Figure 1. Generic mass flow controller (MFC) components and the thermophysical properties required to model them.



Tungsten Hexafluoride

$WF_6$

| M.W. [1] | N.B.P. [2] | T.P. [2] |
|---|---|---|
| 297.84 | 290.25 K | 275.0 K |
| $P_c$ [3] | $T_c$ [3] | $V_c$ [3] |
| 4.57 MPa | 452.7 K | 0.1 $m^3$/kmol |

Return to [Gas Index | Fluid Science Group | Process Measurements Division | NIST Home | SEMI | NSMP ]

| $T$ K | $C_p^0(T)/R$ | Vapor Pressure MPa | $B(T)$ $cm^3 \cdot mol^{-1}$ | $dB/dT$ $cm^3 \cdot mol^{-1} \cdot T^{-1}$ | $C(T)$ $cm^6 \cdot mol^{-2}$ | $dC/dT$ $cm^6 \cdot mol^{-2} \cdot T^{-1}$ | $\lambda$ mW/(m·K) | $\eta$ μPa·s |
|---|---|---|---|---|---|---|---|---|
| Estimated Uncertainty | 1% | 1% | Gas densities are calculated to better than 0.1% over the temperature and pressure ranges of the reference | | | | 10% | 10% |
| Reference | [4] | [6] | [5] | [5] | [5] | [5] | [5] | [5] |
| 205 | 11.84 | 0.19 | -2001.6 | 5951.2 | -4658932 | 47121716 | - | - |
| 210 | 12.00 | 0.34 | -1864.5 | 5441.0 | -3653771 | 36754361 | - | - |
| 215 | 12.16 | 0.58 | -1741.8 | 4994.1 | -2884907 | 28924191 | 5.2 | 14.17 |
| 220 | | 0.95 | -1631.6 | 4600.8 | -2291407 | 22949084 | 5.4 | 14.41 |
| 225 | | 1.53 | -1532.2 | 4252.9 | -1829413 | 18345717 | 5.6 | 14.64 |

**Figure 2.** Sample Web Page from database located at the URL http://properties.nist.gov/semiprop/

**Purpose:** Measure accurately speed-of-sound, viscosity, and Prandtl Number of process gases used in semiconductor processes and dessiminate these to designers and users of mass flow controllers and to the thermal processing modeling community, e.g., modelers of chemical vapor deposition processes.

**Major Accomplishments:** In FY02, we completed speed of sound measurements in the three surrogate gases and the nine process gases listed in Table 1. Typically, the standard uncertainty of the speed of sound was less than 0.01 %. The ideal-gas heat-capacity was determined to within 0.1 % from the zero-pressure intercept of each isotherm. The slope and curvature of each isotherm provided information about each gas's non-ideality from which we developed an equation of state to predict the gas's densities to within 0.1 %.

**Table 1. Ranges of viscosity data.**

| Gas | Temperature Range (K) | Maximum Pressure, MPa |
|---|---|---|
| **He** | **298** | **3.3** |
| **Ar** | **200 - 375** | **3.3** |
| **$N_2$** | **298** | **3.3** |
| **$C_3H_8$** | **225 - 375** | **0.9** |
| **$SF_6$** | **298** | **1.8** |
| **$CF_4$** | **200 - 375** | **3.3** |
| **$C_2F_6$** | **225 - 375** | **2.8** |

The theory of the Greenspan acoustic viscometer was completed. Using this theory, the viscosity results for five test gases agreed within ±0.5 % with reference data. Figure 3 shows the Greenspan viscometer being installed in a facility for handling hazardous gases. Software has been developed to automate and allow safe remote operation of the viscometer. Table 1. lists the seven gases studied in this new facility.

An acoustic resonator optimized to measure the thermal conductivity of surrogate gases and process gases has been designed and fabricated and is currently being characterized with gases of well-known thermal conductivity. The results of this research have been disseminated with seven publications in professional journals and series of talks at professional meetings. Dr. John Hurly is the Technical Editor of the Gases and Facilities Standards Committee of SEMI (Semiconductor Equipment and Materials International). This year, the committee gave Hurly an award for his "outstanding contributions" to the committee's work.

**Figure 3**. The Greenspan viscometer being installed in the new hazardous gases facility.

**Impact:** Gas phase chemical delivery is a fundamental strategy in the manufacture of microelectronic devices. Mass flow controllers (MFCs) are ubiquitous for gas delivery to process chambers. Individual process tools use a significant number (20 - 50) of MFCs to control gas delivery, much of which is in the 1 to 1000 sccm flow rate range. Continued increases in process reproducibility requirements drive the need for improvements in MFC accuracy and stability. Improved thermophysical property data provides the semiconductor industry with the capability to achieve process control with improved accuracy and product reproducibility.

**Future Plans**: During FY03, we plan to:

- Measure the speed out sound in two semiconductor process gases such as $C_4H_8$ and HCl and determine the 'best in the world' equation of state for each fluid.
- Use the Greenspan viscometer to measure the viscosity of three semiconductor process gases such as $N_2O$, HBr, and $NF_3$. For these process gases, for which no viscosity data exist, the uncertainty of the viscosity will be reduced from an estimated 10 % to approximately 0.5 %.
- Design, fabricate, and calibrate an improved Greenspan viscometer, incorporating the lessons learned from our most recent experimental results.
- Improve the acoustic resonator optimized to measure the thermal conductivity, and begin measurements in surrogate gases and process gases.

## Atomic Standard of Pressure

**CSTL Program:** Industrial and Analytical Instruments and Services
**Authors:** *M.R. Moldover, and J. W. Schmidt (836); and K. Szalewicz (U. Delaware)*

**Abstract:** CSTL researchers are developing a novel primary standard for pressure in the range 0.3 MPa – 5 MPa. This will be accomplished both by measuring and calculating the dielectric constant $\varepsilon(p,T)$ of helium with extraordinary accuracy. This new approach to primary standards for pressure will permit the determination of the pressure $p(\varepsilon,T)$ from electrical and temperature measurements to have a smaller uncertainty than the determination of pressure using existing methods to realize standards (piston gages).

**Purpose:** Below 300 kPa, the primary pressure standard at NIST is a mercury manometer. Above 300 kPa, commercially manufactured piston-cylinder sets are used as pressure standards. These sets are complicated artifacts. In operation, the piston must rotate to insure gas lubrication and both the cylinder and piston deform significantly. Thus, piston-cylinder sets must be calibrated against the primary-standard mercury manometer at low pressures and their performance is extrapolated to higher pressures using numerical models of the coupled gas flow and elastic distortions. Piston-cylinder sets exhibit a gas-dependence that is not well understood. Thus, the extrapolation is not fully trusted and it cannot be checked by independent methods above 300 kPa. If the dielectric constant of helium were known accurately enough to serve as a primary pressure standard from 300 kPa to 5 MPa, an independent test of the models used to interpret piston-cylinder sets would be possible.

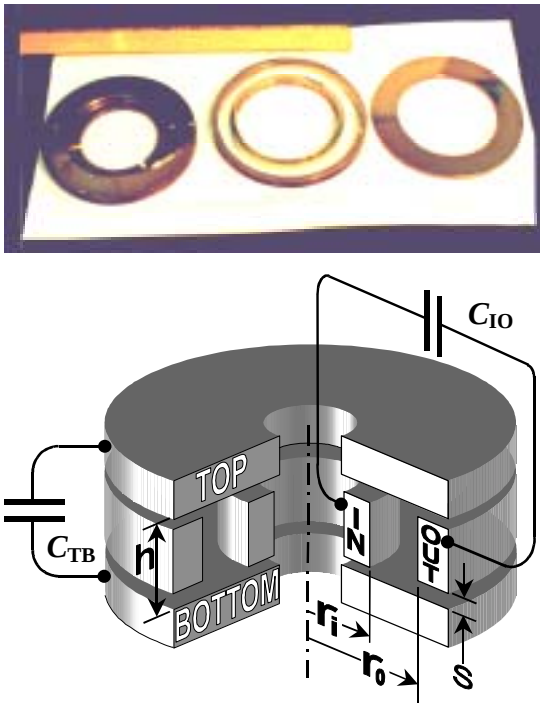



**Figure 1. Toroidal Cross Capacitor and Components**

**Accomplishments:** Dielectric constant measurements are being improved by drawing on NIST's expertise in electrical metrology. Using that expertise, we developed a novel, doughnut-shaped, four-electrode, cross capacitor. (See Fig. 1.) In general cross capacitors are extremely stable electrically and far less subject to surface contamination (oxides, adsorbed water, or films of oil) when compared with capacitors using other geometries. The toroidal design has the further advantage that there are no spurious end effects to complicate the measurements. During FY01/02, the cross capacitor and pressure vessel were tested at 0°C, 30°C and 50°C by measuring the dielectric constant of helium. All of the measured values of $\varepsilon(p,T)$ from two separate cross capacitors of differing designs were consistent with the theoretical values and with each other.

To push the project to the next level of accuracy, four fronts are being attacked simultaneously: (1) improved theory for the dielectric polarizability and virial coefficients of helium, (2) manufacture of cross capacitors with greater stability and larger capacitances, (3), measurement

of the deformation of the capacitors under pressure, and (4) more accurate and versatile capacitance bridges.

CSTL researchers designed a one-piece cross capacitors made from an edge-grown single sapphire crystal. The crystal is hollow with a star-shaped cross section and it has four surfaces that are coated with thin electrodes. Hopefully, single-crystal sapphire capacitors will be more stable than conventional cross capacitors assembled from many metal and insulating parts. Efforts are also under way to fabricate cross capacitors on silicon substrates using MEMS technology.

CSTL has also used cross capacitors to measure the dielectric constants of the primary constituents of natural gas including methane, ethane, propane, nitrogen, carbon dioxide, and argon. The measurements span the 0ºC to 50ºC temperature range and extend to 7 MPa. In this range, these data are more accurate than any previous measurements and provide reference data for use in metering natural gas based on heating value.

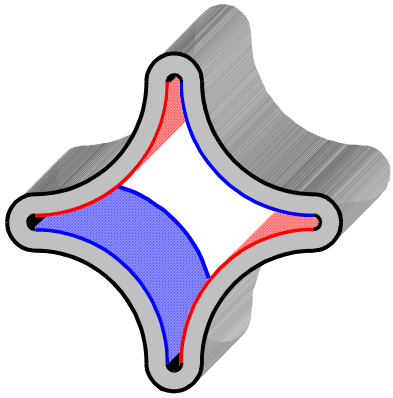


Figure 2. Sketch of single crystal sapphire cross capacitor. Thin-film electrodes are colored blue and red. The prototype will be 25 cm long and 2 cm across its largest extent.

**Impact:** Successful demonstration of the feasibility of absolute pressure measurement standards based on highly accurate knowledge of the dielectric constant of helium has the potential to substantially change realization of primary pressure standards. This work has the potential to provide the basis for improved determination of the Boltzmann constant. Near term impacts derive from the significantly improved measurement of dielectric constant for a range of gases, notably the primary constituents of natural gas. These data are of sufficient accuracy, better than 0.1%, to support new approaches to on-line measurement of heating value of natural gas with significantly greater precision and accuracy and current methods based on chromatographic constituency determination.

**Future Plans:** In FY 03 experiments will focus on the continued development of the cross-capacitor geometry shown in Figure 2 and development of high accuracy capacitance bridge, either at NIST or in concert with commercial vendor(s) in the U.S.

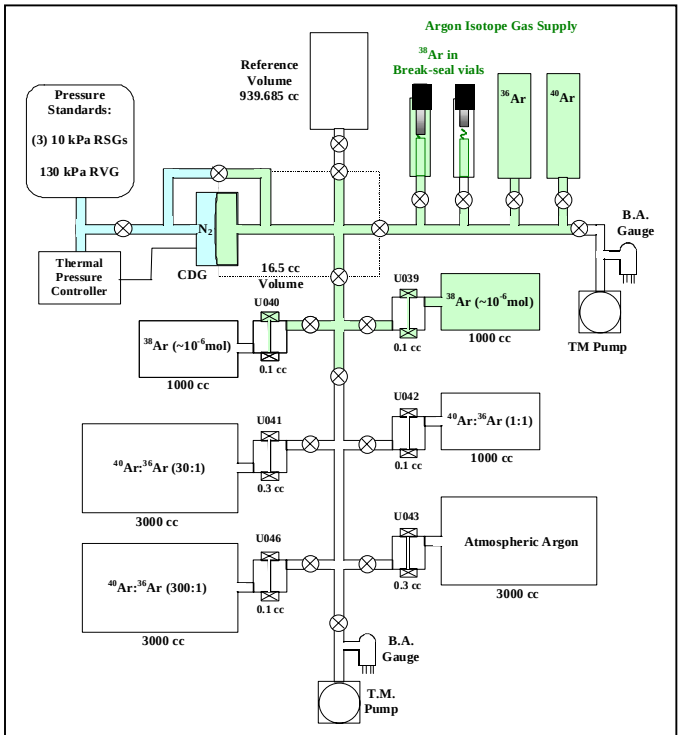
# Development of High-Precision Isotope Reference Standards

**CSTL Program:** Industrial and Analytical Instruments and Services
**Author:** *A.P. Miiller*

**Abstract:** Although conventional K/Ar dating methods are widely used for dating minerals and geologic materials, significant interlaboratory disagreements (1 – 2%) frequently exceed intralaboratory accuracies by an order of magnitude. To improve calibration of the mass spectrometers used, several high-precision argon isotope spike systems have been developed for the U.S. Geological Survey, each consisting of a reservoir and a Dorflinger pipette capable of delivering the required $2 – 4 \times 10^{-10}$ moles per aliquot. Two systems will deliver pure $^{38}Ar$ and three will deliver artificial mixtures of $^{40}Ar/^{36}Ar$ with uncertainties that are expected to be 0.1 – 0.2 % for both amount of gas delivered and for isotopic ratios of the mixtures. The argon spike systems will be used by the USGS to measure the argon concentration of a new preparation of the monitor mineral MMhb-2. This data, when combined with high precision (~0.2 %) potassium concentration data from NIST, will enable the K/Ar age for MMhb-2 to be determined with unprecedented accuracy. The MMhb-2 will be certified by NIST for potassium and argon concentrations and distributed as an SRM, which will be used by argon dating laboratories along with the spike systems to resolve longstanding differences. The spike systems will also enable USGS to re-measure the isotopic composition of atmospheric argon and calculate a new atomic weight for argon.

**Purpose:** Develop several high-precision argon isotope spike systems for the U.S. Geological Survey. This will address the need for accurate standards to calibrate mass spectrometers at major argon-dating laboratories and thus resolve significant disagreements.

**Major Accomplishments**: As per USGS requirements, we delivered portable all-metal spike systems, each consisting of a reservoir and a Dorflinger pipette capable of delivering the required $2 – 4 \times 10^{-10}$ moles per aliquot. Two systems will deliver pure $^{38}Ar$ and three will deliver artificial mixtures of $^{40}Ar/^{36}Ar$ with expected uncertainties of 0.1 – 0.2 % for both amount of gas delivered and for isotopic ratios of the mixtures. The performance of these systems exceeded USGS's expectations by at least a factor of two. The ultra-low fill pressures (~10 Pa) proved to be the major challenge in calibrating the spike systems with requisite accuracy.



System used to calibrate the argon spike systems.

**Impact:** The argon spike systems will be used by USGS to measure the argon concentration of a new preparation of the monitor mineral MMhb-2. This data, when combined with high precision (~0.2%)

potassium concentration data from NIST, will enable the K/Ar age for MMhb-2 to be determined with a 10-fold improvement in accuracy. The MMhb-2 will be certified by NIST for potassium and argon concentrations and distributed as an SRM. The spike systems and the new SRM will be used to resolve differences between argon dating laboratories that have existed for more than two decades. By-products of this research will be the re-measurement of the isotopic composition of atmospheric argon leading to a new atomic weight for argon.

**Future Plans:** Final analysis and report on the spike systems await an impurity analysis of the source gases by the USGS.

# International Comparisons of Pressure Standards

**CSTL Program:** International Measurement Standards
**Authors:** *A.P. Miiller, P.J. Abbott, and A. Lee*

**Abstract:** The status of NIST participation in eight international comparisons of pressure and vacuum standards, at the highest metrological level, is presented. These comparisons help establish degrees of equivalence of national standards from $3x10^{-6}$ Pa to 500 MPa. NIST has piloted three CCM Key Comparisons (two to completion in FY02). The completed comparisons were the first successful international comparisons in this pressure range (1-1000 Pa, absolute and differential modes), and demonstrated general equivalence among the participants, revealed no systematic bias between alternative realizations of the Pascal, and were the only CCM pressure comparisons completed on-time. The third comparison ($3x10^{-6}$ to $9x10^{-4}$ Pa) has completed the measurement phase and is in the analysis and reporting phase.

**Purpose:** Establish degrees of equivalence between national pressure and vacuum standards for pressures from $3x10^{-6}$ Pa to 500 MPa. 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 pressure and vacuum measurement standards needs to be assessed, established, formally recognized, and maintained.

**Major Accomplishments:** The prevailing CCM Key Comparisons in pressure are listed in the table below.

| Comparison Number | Pressure Range | Transfer Standard | Status | Pilot NMI* | Participants* |
|---|---|---|---|---|---|
| CCM.P-K1.a, b | 0.05 - 1 MPa (gauge) | Piston Gauge | Approved | a-6<br>b-3 | 1ab, 2a, 3ab, 5ab, 6ab |
| CCM.P-K1.c | 0.08 - 7 MPa (gauge) | Piston Gauge | Approved | 5 | 1, 2, 3, 4, 5, 6 |
| CCM.P-K2 | 10 – 120 kPa (absolute) | Piston Gauge | Analysis & Reporting | 2 | 1, 2, 5, 6, 10, 12, 13, 14, 15, 16, 17, 18 |
| CCM.P-K3 | $3x10^{-6}$ - $9x10^{-4}$ Pa (absolute) | Spinning Rotor and Ion Gauges | Analysis & Reporting | 1 | 1, 2, 5, 7, 8, 9 |
| CCM.P-K4 | 1 - 1000 Pa (absolute) | Low Pressure Transducers | Approved | 1 | 1, 2, 5, 7, 8, 9, 10 |
| CCM.P-K5 | 1 – 1000 Pa (differential) | Low Pressure Transducers | Approved | 1 | 1, 2, 5, 10, 11 |
| CCM.P-K6 | 10 – 120 kPa (differential) | Piston Gauge | Analysis & Reporting | 2 | 1, 2, 5, 6, 10, 13, 14, 15, 16, 17, 18 |

*Legend of NMIs:

1. National Institute of Standards and Technology (NIST) – U.S
2. National Physical Laboratory (NPL) – United Kingdom
3. Laboratoire National D'Essais (LNE) – France
4. National Research Laboratory for Metrology (NRLM) – Japan
5. Instituto di Metrologia "G Colonnetti" (IMGC) – Italy
6. Physikalisch-Technische Bundesanstalt (PTB) – Braunschweig, Germany
7. Physikalisch-Technische Bundesanstalt (PTB) – Berlin, Germany
8. Korean Institute of Standards and Science (KRISS) – S. Korea
9. National Physical Laboratory (NPLI) – India
10. Commonwealth Scientific and Industrial Research Organization (CSIRO-NML) – Australia
11. Measurement Standards Laboratory (MSL) – New Zealand
12. Bureau International des Poids et Mesures (BIPM)
13. Insitut National de Metrologie (INM) – France
14. National Research Council (NRC) – Canada
15. Nederlands Meetinstituut (NMi) – Netherlands
16. Office Fédéral de Métrologie (OFMET) – Switzerland
17. National Institute of Metrology (NIM) – China
18. D.I. Mendeleyev Institute for Metrology (VNIIM) – Russian Federation

Comparisons CCM.P-K4 and CCM.P-K5 were formally approved by the CCM in FY02. Their results were presented in last year's FY01 report, but to summarize, the completed comparisons were the first successful international comparisons in this pressure range (1-1000 Pa, absolute and differential modes), and demonstrated general equivalence among the participants, and revealed no systematic bias between alternative realizations of the Pascal. In recognition for overcoming major technical and engineering barriers in developing robust, state-of-the-art low-pressure transfer standards that enabled the successful completion of these two precedent-setting comparisons, A. P. Miiller was awarded the 2002 CSTL Technical Achievement Award. He was also appointed to the Chair of the Low-Pressure Working Group of the CCM. Comparison CCM.P-K3 is also piloted by NIST. The transfer-standard package that was developed at NIST, consists of two spinning rotor gauges, three Bayard-Alpert ionization gauges, and began circulation in FY99. The comparison is behind due to delays between participants, but measurements were completed in FY02, although some participants have not yet submitted their results.

**Impact:** CCM.P-K4 and -K5 have formally established the degree of equivalence between several NMIs in an industrially important pressure range. Despite over a decade of attempts, -K4 and -K5 are the first successful comparisons in this range, have unambiguously established degrees of equivalence between NMIs, and revealed no significant relative bias among the different techniques to realize the Pascal from 1 to 1000 Pa. The innovative transfer package developed for this comparison has formed the basis for many variants in regional comparisons throughout the world.

**Future Plans:** In FY03, we expect to complete the Draft A (preliminary analysis) report of CCM.P-K3. In addition, we shall continue to promote participation in SIM regional comparisons to tie other SIM countries into the CCM results. For FY03, significant funds will be re-programmed from CCM comparisons into support for SIM comparisons.

**Publications**: Miiller, A. P., Bergoglio, M., Bignell, N., Fen, K. M. K., Hong, S. S., Jousten, K., Mohan, P., Redgrave, F. J., and Sardi, M., *Final Report on Key Comparison CCM.P-K4 of Absolute Pressure Standards from 1 Pa to 1000 Pa*, Metrologia 39, Tech. Suppl. 07001 (2002). Miiller, A. P., Cignolo, G., Fitzgerald, M. P., and Perkin, M. P., *Final Report on Key Comparison CCM.P-K5 of Differential Pressure Standards from 1 Pa to 1000 Pa*, Metrologia 39, Tech. Suppl. 07002 (2002).

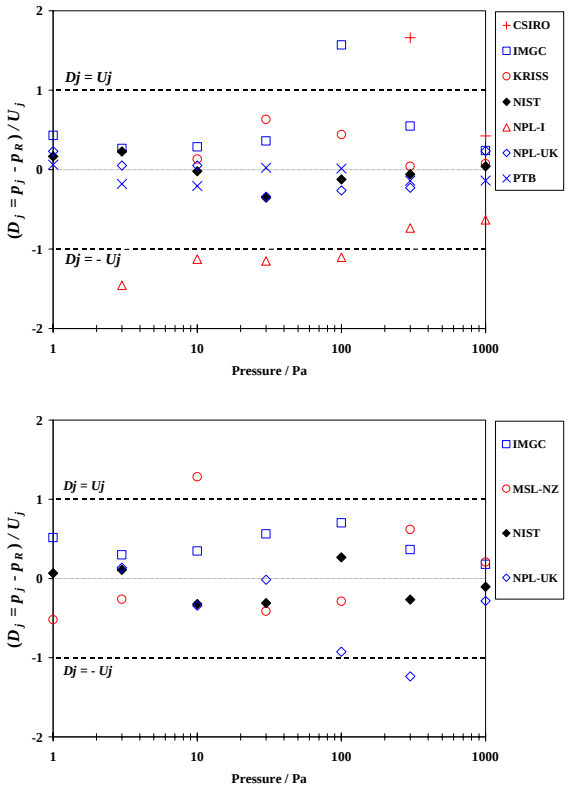



**Figure 1.** Results for CCM.P-K4 (upper) and –K5 (lower): the deviation of National Metrology Institute j from the reference value divided by the uncertainty of this deviation (at a 95% level of confidence).

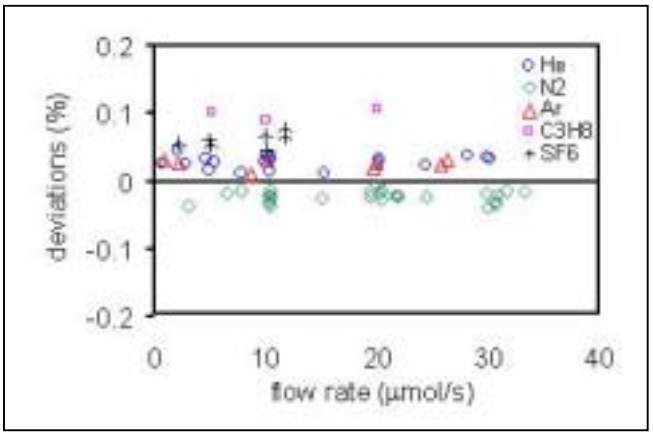
# Measurements for Vacuum Process Control

**CSTL Program:** Microelectronics
**Author:** *R.F. Berg*

**Abstract:** The semiconductor electronics industry uses thermal mass flow controllers (MFCs) to control processes such as plasma etching. A wide variety of toxic, flammable, and corrosive gases are used at flow rates below 1000 μmol/s. (1 μmol/s ≈ 1.3 standard $cm^3$/min.) This variety challenges the companies that manufacture and calibrate MFCs. In 2000, participants at an MFC workshop at NIST predicted that industry requirements for flow uncertainty will fall below 1%, and they called for corresponding improvements of national standards. In response, we are developing and improving standards for gas flow in the range from 0.01 to 1000 μmol/s.

**Purpose:** Develop improved gas flow rate standards addressing the need of the semiconductor industry for more accurate MFC performance. We are following the recommendations of the MFC workshop by (1) improving the uncertainties of primary and transfer standards for gas flow to 0.025 % and 0.1 % respectively, and (2) widening the range of transfer standards to 0.01 to 1000 μmol/s. We are using international flow comparisons to verify the NIST standards and domestic flow comparisons to assist US industry.

**Major Accomplishments:** We have developed a flow metering approach based on capillaries as a a transfer standard having improved reproducibility. The capillary flow meter (CFM) is a second-generation transfer standard whose flow elements consist of long, coiled, quartz capillaries. A hydrodynamic model of the CFM standard has been developed and validated against two primary flow standards. Tests with nitrogen agreed with both primary standards at flow rates from 0.1 to 1000 μmol/s. Tests with other gases verified that the model correctly handles gases with widely varying thermophysical properties. A comparison with Italy's metrology institute (IMGC) showed agreement to within 0.1 % from 0.2 to 800 μmol/s. Flow comparisons with two US manufacturers of gas flow standards tested each company's primary standards to high accuracy and demonstrated NIST's emerging capability to measure small gas flow rates with excellent precision and accuracy.




**Impact:** The improved model of the CFM extended the transfer standard's usefulness to a wide variety of gases. One of the domestic flow comparisons helped identify an important improvement for the company's flow standard.

**Future Plans:** We are constructing a third-generation transfer standard that is easier to use and more rugged. The goal is to provide a transfer standard that can be operated offsite by an industrial customer, with NIST providing assistance by phone, email, or an Internet web data link.

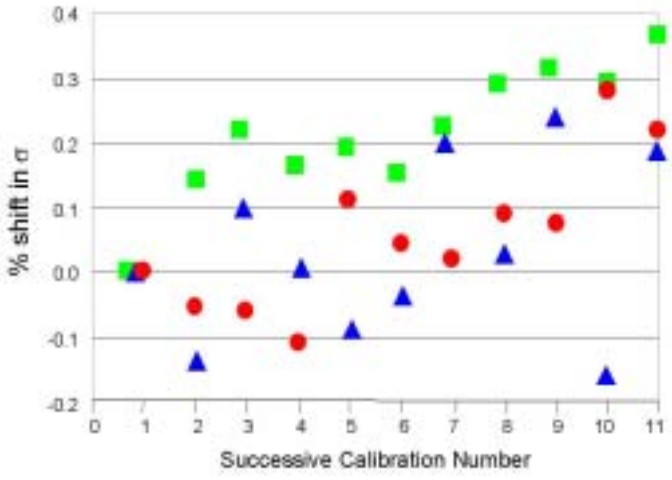
# Improved Vacuum Transfer Standards

**CSTL Program**: Industrial and Analytical Instruments and Services
**Author***: R.F. Chang*

**Abstract**: Our goal is to disseminate NIST's realization of the Pascal at high vacuum levels directly to our customers and into widely used commercial gauges. However, commercial vacuum transfer gauges are unstable and hamper efforts to effectively disseminate NIST's uncertainties to its customers. In FY02, we identified the causes of instabilities in spinning rotor gauges (SRGs), which are one of the more stable type of vacuum transfer gauges. We quantified the effect of several factors on the accommodation coefficient (σ) of SRGs, which is directly tied to gauge calibration. De-mounting and re-mounting of the suspension head caused a 0.1% shift in σ, which was comparable to the difference between baked and unbaked systems. Surprisingly, sudden loss of rotor suspension did not have any measurable effect on σ, contrary to long-held belief. This work quantified the effects of several factors for the first time, but even taken in total, cannot explain some of the larger instabilities observed in customer gauges

**Purpose**: The spinning rotor gauge (SRG) has become the transfer standard of choice for vacuum calibrations from $10^{-4}$ to 1 Pa due to good calibration stability (changes < 0.5%/year). While internal NIST SRGs exhibit even better long-term stability, some gauges of calibration customers have shown inexplicably large shifts. In FY02 we began a series of tests to quantify the effects of several potential sources of gauge instability. Explanation of these instabilities is important for gauge users and manufacturers, but also to identify problems for a new on-demand NIST service envisioned to provide pre-calibrated rotors for SRG customers.

**Major Accomplishments**: Three factors believed to strongly affect SRG calibration stability were quantified: de-mounting/re-mounting of the SRG suspension head; sudden loss of suspension of the rotor; and baked vs. unbaked gauges. These factors were also selected because they typify the treatment of gauges and rotors of many calibration customers after they leave NIST. The effect of removing, then remounting, the magnetic suspension head of the SRG caused an average shift of ~ 0.1%. This was previously thought to have a negligible effect. However, the sudden loss of magnetic suspension was thought to cause a large shift in calibration, but results demonstrated little change. We also investigated unbaked rotors as many customers do not bake their SRG vacuum systems. This was also thought to cause a large shift as surface absorbed water would not have been removed without a baking process. Although a difference of ~ 0.1% was observed, this was smaller than expected.




Three SRGs show an average of ~0.1% (0.4% max.) shift in calibration stability between 11 successive mountings and de-mountings.

**Impact**: Quantitation of these effects on SRGs has not been documented before, and in fact, goes against commonly held beliefs about their performance in the mid-range vacuum community. Our results can significantly affect the treatment and operation of all SRGs, and will provide the basis for developing an uncertainty budget for our proposed on-demand SRG rotor calibration service.

**Future Plans**: Additional aspects to explore include effects of magnetic polarization and other surface treatments upon the calibration stability of SRGs. This information will likely explain the remaining large calibration shifts observed by some customers, and also provide more data to help investigate the feasibility of an on-demand SRG calibration service.

# Transducer-Assisted Piston Gauge Calibrations

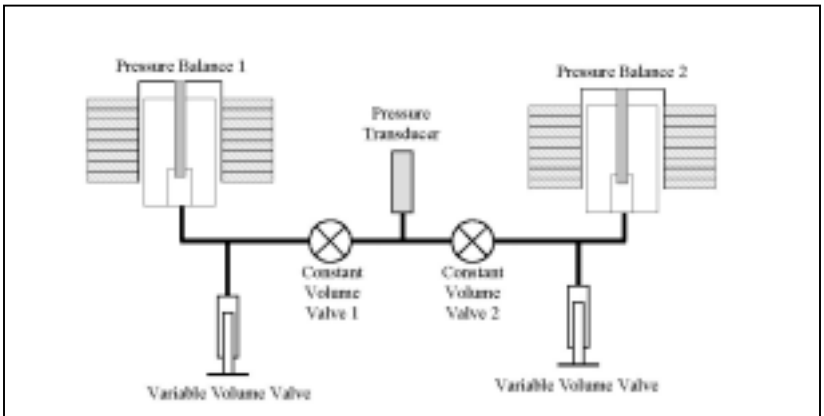
**CSTL Program:** Industrial and Analytical Instruments and Services
**Authors:** *D. A. Olson (836); and T. Kobata (NMIJ, Japan)*

**Abstract**: A method to automate the data-gathering process in the calibration of one piston gage against another has been developed. Rather than adjusting small "trim" masses until the balances generate equal pressure, the two balances are brought into approximate pressure equilibrium and a pressure transducer measures the remaining pressure difference. This approach has been successfully demonstrated from 20 to 200 MPa on a hydraulic system and resultant uncertainties compare very favorably with the prevailing fall-rate method. This method improves piston gauge calibrations by reducing or removing operator judgment and manual data entry, and introduces more consistency through automation, with no penalty in overall uncertainty.

**Purpose**: Existing piston gauge calibration methods require a great deal of operator skill and experience to find a pressure balance point and render a decision about when the equilibrium is "sufficient" so that the next datum can be set and acquired. Our objective is to improve piston gauge calibrations by reducing or removing operator judgment and manual data entry, and introduce more consistency through automation, with no penalty in overall uncertainty.

**Major Accomplishments**: The transducer-assisted traditional fall-rate methods have been demonstrated to agree with the combined standard uncertainty of the methods in nearly all cases, and to within the combined expanded uncertainty (k=2) for all cases. The combined standard uncertainties for this method are 53-112 Pa, making them on the same order as the resolution of the pressure transducer (56 Pa). The relative combined standard uncertainties are $3.6 \times 10^{-6}$ or less at 20 MPa, and $1.1 \times 10^{-6}$ or less above 50 MPa, and compare quite favorably with the relative combined standard uncertainty of the NIST Transfer Standard at 280 MPa, which is $16 \times 10^{-6}$ (k=1). To keep the uncertainty in the method comparable to the uncertainty of the fall rate method, the pressure difference between the two piston gauges, in this case, was $|\Delta P| \leq 10^5$ Pa, which keeps the transducer uncertainty equal to or less than other component uncertainties. An unexpected advantage of the transducer-assisted method is far greater sensitivity over extant methods, which also allows us to observe 2nd-order effects such as effective area dependence on piston stroke height. Thus, we have achieved our objective to improve piston gauge calibrations and introduce more consistency through automation, with no penalty in overall uncertainty.

**Impact**: The transducer-assisted method has already impacted NIST calibration services and allowed us to discover systematic problems in a recently purchased piston gauge that could not have been noticed using traditional calibration methods.



Schematic of hardware set-up for Transducer Assisted Calibration

Widespread adoption of this straightforward method will provide piston gauge

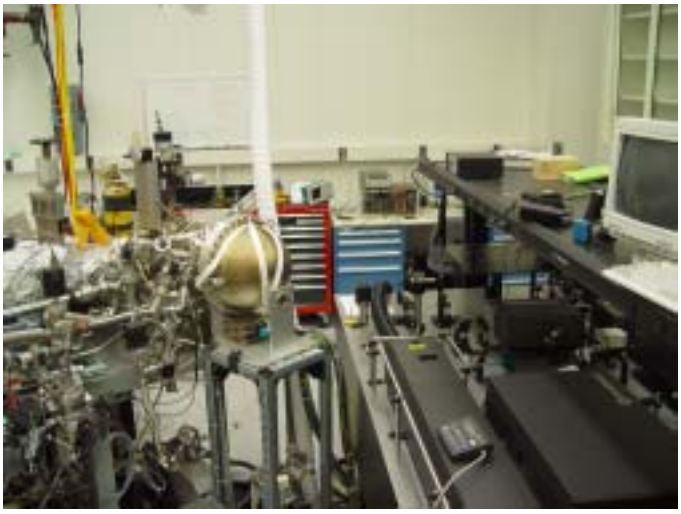
manufacturers a far more sensitive diagnostic tool than ever before available, and could culminate in substantive performance improvements for this mature field.

**Future Plans**: The transducer-assisted method will be incorporated into NIST hydraulic piston gauge calibration services. This method will be studied on NIST pneumatic piston gauge calibrations to see if similar gains can be made.

# Electronic Structure and Transport in Model Molecular Electronic Systems

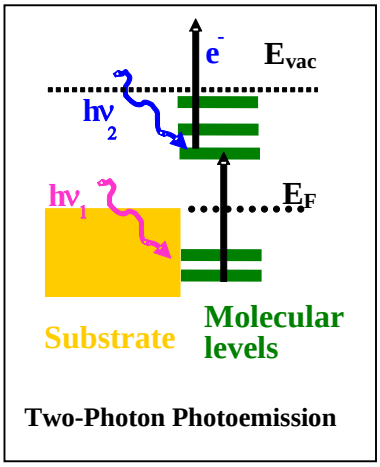
**CSTL Program:** Technologies for Future Measurements and Standards
**Authors:** *J.D. Batteas, S.W. Robey, R.D. Van Zee, and C.D. Zangmeister*

**Abstract**: The drive to increase electronic device performance, with the associated push to ever smaller device dimensions, has lead industry observers to conclude that silicon-based technology will reach a point of diminishing gains in the near future. This, in turn, has generated interest in alternatives technologies based, for instance, on single-electron devices and molecular components. It is hoped that the tremendous flexibility available with organic synthetic chemistry and self-assembly techniques can be harnessed to produce non-linear devices analogous to silicon-based diodes and transistors, but comprised of single or small numbers of molecules. The CSTL effort in molecular electronics is developing a battery of techniques that will provide necessary information on electronic structure and electron transport in candidate molecular electronic systems. The methods being used include two-photon photoemission, which accesses unoccupied electronic levels and tracks electron relaxation effects, and scanned probed techniques, which can characterize electron transport down to the single molecule level.

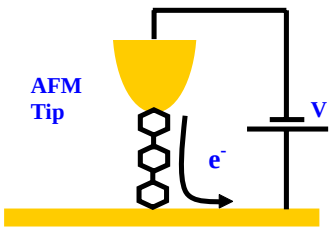


**Purpose:** This work will develop measurement techniques and expertise necessary to understand electronic structure and dynamics in mesoscopic systems comprised of organic thin films and small molecular aggregates. The overall goal is to provide information that, when coupled with theoretical input, will help to illuminate the physical mechanisms that produce the useful, non-linear effects observed in molecular electronics device-prototypes. This information is also required to develop measurement standards and test protocols for such devices.

**Major Accomplishments:** We have been primarily validating the performance of laboratory instrumentation against well-characterized systems. An ultrahigh vacuum analysis system was assembled and coupled to a femtosecond Ti:sapphire laser for studies of electronic structure using two-photon photoemission. A scanned-probe system was purchased and Dr. James D. Batteas was hired to lead investigations of the structure and transport properties in model molecular electronics systems. Preliminary studies of d-c transport through small numbers of conjugated molecules were also begun.




**Two-Photon Photoemission**




**Scanned Probe Transport**

**Impact:** This project is poised to begin providing results that will lead to a more complete understanding of electronic structure and transport effects in molecular electronic systems. These results will benefit the development not only of potential molecular electronics applications, but will also find use in current technologies using organic molecules in electronic applications such as light emitting diodes and field effect transistors.

**Future Plans:** In coming years, we will study the electronic structure and conduction properties of a series of molecules from the oligio-(phenyl-ethnyl) family of molecules. These experiments will include conventional and multi-photon electron spectroscopies conducted on films of these molecules. The scanned-probe instrument will be used to study the conduction properties of small aggregates of conductive molecules. The structural and conduction properties of these pads will be compared to those of large areas films. The results from these experiments will be compared to theoretical models develop by our collaborators in the Physical and Chemical Properties Division and to the performance of device-prototypes fabricated and tested by our collaborators in the Semiconductor Electronics Division.

# DNA and protein gel plugs for biological assays

**CSTL Program:** Health and Medical Products and Services
**Authors:** *R. Zangmeister, G. Thomas, D.J. Ross, and M.J. Tarlow (836); and K. Olsen (Loyola College*

**Abstract:** A new method for immobilizing biological capture ligands in microfluidic devices has been devised by the Process Sensing Group (PSG) with potential for use in disease diagnosis, and high throughput genomics and proteomics. In the method, ligands such as DNA or proteins are covalently bound in a porous acrylamide gel plug that is formed in microfluidic channels by photo-polymerization. DNA or proteins that flow through the plugs can be captured by an appropriate ligand and then detected. Multiple plugs, each containing a different biological ligand and spatially separated from each other, can be formed in the same channel, which enables the simultaneous analysis of many DNA and protein molecules. Primary advantages of using gel plugs in microchannels include more efficient capture of biological species versus bulk solution methods, enhanced mass transfer of the analytes, and exploitation of novel, flow directional capabilities of microfluidic devices, all leading to greater analytical sensitivity for a variety of assays.

**Purpose:** Develop new transduction approaches for chemical and bio-chemical analyte concentration measurement in microfluidic systems.

**Major Accomplishment:** The PSG has devised a new, versatile method for securing biological ligands in microfluidic devices for a variety of biomedical assays. One such assay involves hybridization of nucleic acids for DNA sequence determinations. Single stranded DNA (ssDNA) probes modified on one end with an acrylamide functional group are photo-polymerized with polyacrylamide, creating a stable gel matrix with the ssDNA covalently bound. Complementary single stranded sequences, or targets, that are electrophoretically driven through such probe containing gel matrices are captured, while non-complementary targets migrate through. The high concentration of the probes in the gel plugs coupled with the enhanced mass transfer characteristics of microfluidic channels ensure that targets will encounter a complementary probe, be captured, and thus be detected. Spatially distinct gel plugs each containing a different probe sequence can be formed photo-lithographically in a single channel for simultaneous detection of multiple targets. In addition, a parallel effort this year demonstrated a conceptually similar approach for antigen capture assays where antibodies were entrapped in photo-polymerized gel-plugs. Specific antibody/antigen interactions using target and non-target antigens were demonstrated with the

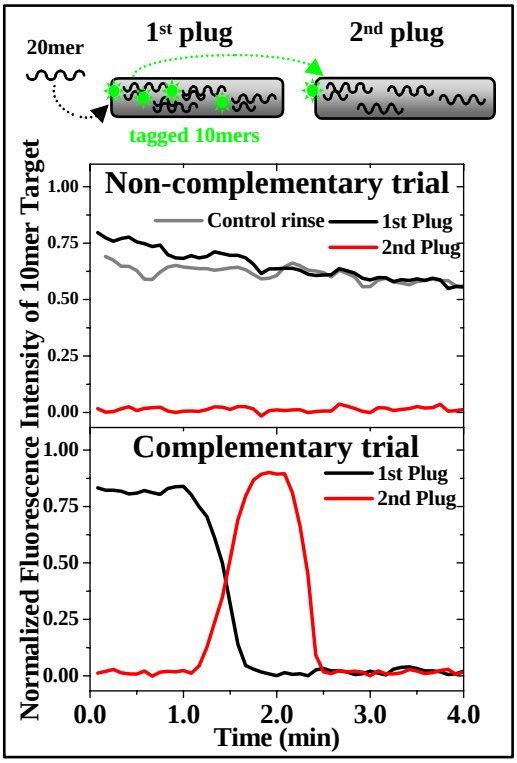



**Figure 1.** Scheme for competitive DNA assay using probe (1st plug) and capture (2nd plug) gel plugs. Plots of fluorescence intensity measured of tagged 10mer initially hybridized in gel plug 1 during electrophoresis of both complementary and non-complementary 20mer targets.

hydrogel-entrapped antibodies. Future work is expected to demonstrate enhanced utility of gel-plugs to applications involving catalytic DNA. A novel two-plug probe/capture strategy will be used in conjunction with catalytic DNA for the detection of Pb in water. A paper describing the formation and use of DNA gel plugs was published in Analytical Chemistry in 2002.

# Temperature Gradient Focusing

**CSTL Program**: Health and Medical Products and Services
**Authors***: D. Ross (836); and L.E. Locascio (839)*

**Abstract:** To meet the outstanding need for effective pre-concentration techniques for microfluidics, a new focusing method, Temperature Gradient Focusing (TGF), was invented. Initial experiments indicate that the new method has great promise as a technique for the pre-concentration (greater than 10,000-fold concentration demonstrated) as well as for the focusing and separation of a variety of charged analytes including fluorescent dyes, amino acids, proteins, DNA, and colloidal particles.

**Purpose:** This project was initiated to address one of the outstanding problems in the field of microfluidics: the need for an effective method of pre-concentration that is suitable for miniaturization and integration into "lab-on-a-chip" platforms.

**Major Accomplishments:** The major accomplishment on this project for fiscal year 2002 was the invention of TGF, a new method for the focusing and concentration of charged analytes in microfluidic channels or capillaries. TGF operates by balancing the electrophoretic motion of analytes in a micro-channel against the bulk flow of buffer solution through the channel while applying both an electric field and a temperature gradient along the channel. If the ionic strength of the buffer solution is temperature-dependent, the temperature gradient will give rise to a corresponding gradient in the electrophoretic velocity of a charged analyte in the channel. The bulk flow velocity can then be adjusted so that the total analyte velocity (the sum of the bulk and electrophoretic velocities) is zero at some point along the channel, and all of the analyte will be focused at that point. As a method for analyte pre-concentration, TGF out-performs all other methods, with demonstrated concentration factors exceeding 10,000. Further, it is relatively simple compared with other pre-concentration methods, making it particularly well suited to integration into "lab-on-a-chip" devices. In addition to analyte pre-concentration, TGF can be used for the separation of different charged analytes in a manner analogous to isoelectric focusing of proteins. TGF is much simpler to implement than isoelectric focusing and has the additional advantage that it can be used with any charged analyte, rather than just proteins. This versatility is shown graphically in Fig. 1 with separations of a variety of analytes.

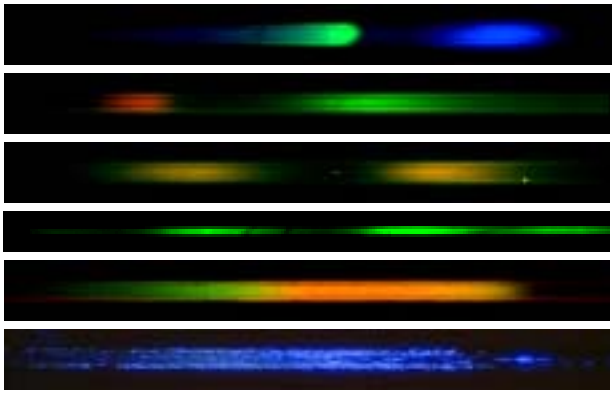


Figure 1. Demonstration of TGF for the focusing and separation of (from top to bottom) small fluorescent dyes, amino acids, proteins, DNA, and colloidal particles.

**Impact:** The initial publication describing the new method has been well received, and it has been the subject of oral presentations at all of the major microfluidics conferences during the last year.

**Future Plans:** Because of the promising nature of the initial demonstrations of TGF, research on this project will continue with emphasis on proving the method further by applying it to current problems in analytical chemistry and biochemistry.

# Development of Process Monitoring and Diagnostic Techniques

**CSTL Program**: Microelectronics

**Authors:** *M. Sobolewski, and K. Steffens (836); and E. Benck (842)*

**Purpose:** The goal of this project is to develop advanced measurement methods, data, 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. 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 an important 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.

**Major Accomplishments:** We published a rigorous experimental validation of model predictions for ion kinetic energy distributions in $CF_4$ discharges in a high-density plasma reactor. The model was found to accurately predict ion energy distributions including their dependence on rf bias amplitude, rf bias frequency, total ion flux, and ion mass. We developed and tested a model-based technique for monitoring ion energy distributions that relies on rf current and voltage measurements made outside of a plasma reactor. The technique is designed for process monitoring applications in manufacturing where the use of invasive probes to measure ion energies is not practical. As model-based reactor design and process development become increasingly utilized, species density measurements and gas temperatures can provide important input and validation for plasma modelers. In dielectric etching plasmas, CF is an important species to understand because it is thought to participate in the formation of the fluorocarbon polymer layer which enables selective etching of $SiO_2$. Planar laser-induced fluorescence (PLIF) has been used to measure two-dimensional density maps of CF as a function of power and pressure in $CF_4/O_2$ and $C_4F_8$ plasmas and as a function of power in $CF_4$ with and without a Si wafers. Spatial variations in plasma temperature can cause spatial differences in gas density and reaction rates. Thus, understanding gas temperature in etching plasmas is also important. The technique of PLIF of the CF radical has been extended to enable two-dimensional temperature mapping in fluorocarbon plasmas. Temperature maps have been measured in $CF_4$ plasmas from 200 to 800 mTorr. Temperature spatial variations of up to 150 K have been observed in these plasmas. Temperature increases with pressure and power is is lowest near the cooled electrode surfaces.

**Impact:** Measurement techniques, data, and models provided by NIST continue to assist our customers in industry to improve their plasma modeling and characterization efforts. Recent examples include NIST-developed electrical analysis techniques that are used by an equipment manufacturer to improve tool-to-tool reproducibility, and the web-based NIST electron interactions database which distributes fundamental data to plasma modelers in industry and academia world-wide.

**Future Plans:** Future plans include the further development of model-based process monitoring techniques, and continuing efforts to adapt our plasma reactors to operate in the dual-frequency capacitively coupled mode used in state-of-the-art, industrial oxide etchers.

# Chemical Analysis Through Rapid Micro-Boiling Events

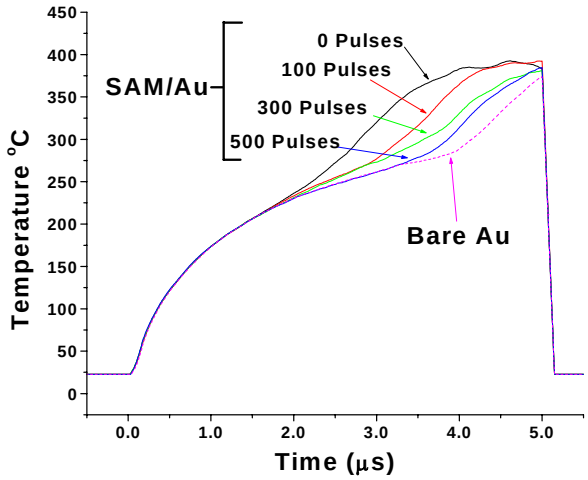
**CSTL Program:** Health and Medical Products and Services

**Authors:** *O. Thomas, R.E. Cavicchi, and M.J. Tarlov*

**Abstract:** A new electrical measurement method has been developed that is sensitive to the wetting properties of surfaces and the chemical composition of liquids. In this technique, thin film microheaters (μHs) immersed in a fluid are heated using a voltage pulse of 2-10 microseconds in length. Using the μH as a resistance thermometer, micro-boiling of the liquid, AKA bubble nucleation, is detected as a change in the heater temperature during the voltage pulse due to the difference in the thermal conductivity of the vapor versus the liquid. Complex micro machined devices are not required; the measurement can be performed with structures as simple as a thin metal line on a substrate. The measurement is novel, easy to perform, and fast. The technique has potential for the detection of surface binding events such as those found in gene and protein chips.

**Purpose:** Develop new methods for in-situ measurements in microfluidic systems.

**Major Accomplishment:** A new technique based on rapid microboiling events has been devised that is sensitive to the topmost molecular layer of a μH used to initiate boiling and the chemical composition of the liquid that boils. The idea for the method came from previous studies of ink-jet printing and steady state pool boiling. These reports suggested that boiling, or bubble nucleation, initiated by rapidly heated μHs might depend sensitively on the wettability of the heater surface, as well as properties of the liquid such as viscosity, surface tension, and chemical composition. The μHs used here are ~1 μm thick films of Pt or Au-plated Pt with dimensions of ~ 3 X 200 μm. The micro-heaters are immersed in water and rapidly heated with short (<10 μsec) square voltage pulses. Temperature-time transients of the microheaters are recorded by measuring the heater resistance during the application of the heating pulse. The bubble nucleation event, i.e., boiling, is signaled in the transient by an inflection point that results from a change in the rate of heat transfer to the liquid when a vapor bubble forms on the heater. Parameters such as nucleation temperature and average heater temperature are determined from the transients. In experiments where trace amounts of a neutral surfactant, triton X-100, were added to water, average heater temperatures determined from temperature-time transients were dramatically higher and ppm levels of the surfactant were easily detected. More importantly, using alkanethiol self-assembled monolayers (SAMs) to control the wettability of Au μHs, dramatically different transients were obtained from bare Au μHs and those modified with hydrophobic and hydrophilic SAMs. The




Temperature-time transients of a bare Au micro-heater and the same micro-heater modified with a hydrophobic octanethiol [$CH_3(CH_2)_7SH$] alkanethiol SAM as a function of pulse number demonstrating that a single molecular monolayer alters bubble nucleation at a surface.

significance of these results is that it may be possible to detect biological binding events by measuring changes in bubble nucleation due to alteration of surface wetting properties. If a binding event can be shown to alter bubble nucleation, then a simple, fast, low cost electrical detection method suitable for gene and protein chips, and lab-on-a-chip applications may be possible. Future work will explore the feasibility of this strategy.

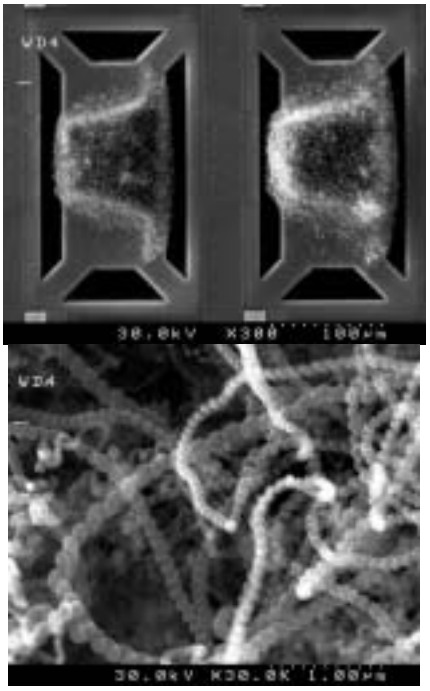
# Carbon Nanotubes (CNTs) on Microhotplates

**CSTL Program:** Industrial and Analytical Instruments and Services
**Authors:** *R.E. Cavicchi, C. Montgomery, and C.J. Taylor*

**Abstract:** CNTs are finding an increasingly broad range of applications based on their high aspect ratio, excellent electrical and thermal conductivity, and mechanical strength. For electronic applications, fabrication research has focused on chemical vapor deposition involving the decomposition of an organic gas over a dispersed catalytic metal in a hot wall reactor. This work demonstrated for the first time the use of localized heating created by a microhotplate (μHP) in a cold CVD system to selectively deposit nanotubes on a microscale area. A combinatorial study was performed in which different elements of a 340 element array were exposed to different process conditions such as growth temperature and amount of metal catalyst. The work demonstrates that MEMS-based microheaters can be efficient combinatorial platforms for optimizing the fabrication of nanomaterials. Other applications include chemical sensing, display technology, and molecular electronics.

**Purpose:** Develop new methods and techniques and investigate new materials supporting investigation of transduction strategies for measurement of gas phase, chemical species.

**Major Accomplishment:** CNTs represent an important class of nanophase materials which have a broad range of potential applications in electronics, such as chemical sensors, flat panel displays and other field-emission devices, and molecular-scale electronics. For chemical sensing the appeal of these materials is their high surface-to-volume ratio, and their excellent electrical and thermal conductivity, all useful properties for conductance and calorimetric-based sensors.



Top: selective growth of carbon nanotubes on microhotplates.

Bottom: magnified view.

A large variety of CNTs can be produced by different CVD processes: single or multiwalled nanotubes, varied radius and chirality, and defect-induced shapes such as rods, ropes, and coils. Many applications also may have a thermal budget, in which some components on the substrate cannot tolerate the high temperatures (500 – 1000 °C) needed to fabricate CNTs. Here we describe a CNT fabrication method that works around the thermal budget problem, is an efficient CNT combinatorial research platform, and has the potential for use in chemical sensing.
Using μHP arrays consisting of 4, 16, and 340 elements, CNTs were grown under a variety of process conditions using different catalysts, organic precursors and process conditions. The 340 element array was used to perform a combinatorial study. Eight different thickness of a Ni catalyst were combined in a matrix of samples to explore pre-anneal conditions, growth temperature, and growth pressure. The films were characterized by scanning electron microscopy. The figures show patches of CNTs

localized on two elements of the array and coiled nanotubes that are observed under higher magnification. The results indicate the range of conditions needed to produce different types of carbon nano-structures from rods, to coils, to metal-centered carbon clusters.

**Impact:** This work sets the stage both for future combinatorial work, and for developing a CNT-based technology in which high temperatures are generated by μHPs and growth is local. The efficiency of combinatorial studies may accelerate the progress towards what has been termed the "holy grail" of process condition definition that would selectively grow CNTs of a chosen chirality and diameter. The ability to grow these structures on μHPs opens the way towards building chemical sensors that use the beneficial properties of CNTs.

**Future Plans**: Work in the coming year will include further studies for using CNTs as templates to grow other materials and as chemical sensors.

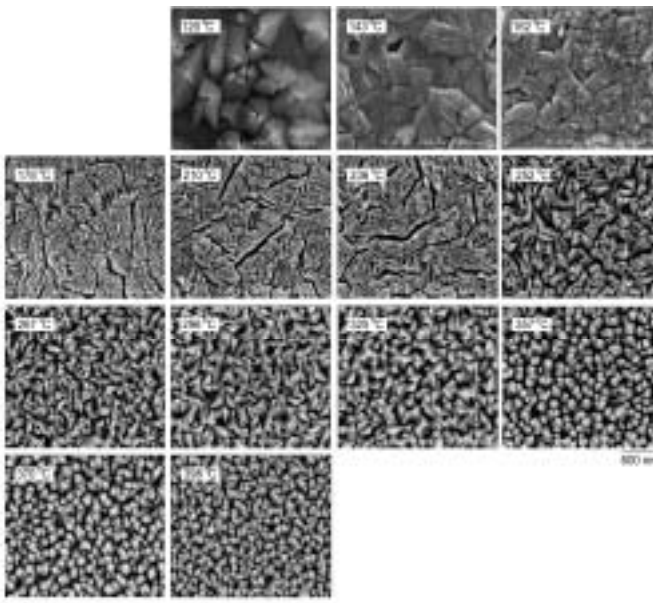
# Efficient Development of Materials for Chemical Sensing Using MEMS-Based Microarrays

**CSTL Program**: Industrial and Analytical Instruments and Services
**Authors:** *C.J. Taylor, D.C. Meier, and S. Semancik*

**Abstract:** Special types of thin film materials are required to perform various functions within chemical microsensors and microanalytical systems. Sensing materials, for example, must be tailored to detect the specific gases encountered in chosen application areas with sufficient sensitivity, selectivity and speed. Other examples include preconcentrator and separator materials where chemical and microstructural properties must allow preferential adsorption or reaction at large number of surface sites. A combinatorial approach using MEMS-based microarrays has been developed to efficiently deposit and screen thin film sensing materials for detection of chemical warfare agents and planetary gases in projects funded by the Defense Threat Reduction Agency (DTRA) and NASA, respectively.

**Purpose:** Explore chemical sensing properties of metal oxide materials using combinatorial methods for characterizing sensitivity, selectivity, and stability in sensing applications.

**Major Accomplishment**: We have developed a combinatorial-based approach using MEMS microarrays to efficiently screen films deposited by chemical vapor deposition (CVD) for chemical sensing applications. Films of gradually varied composition and microstructure are deposited on an array by holding each element of the microarray at a different temperature. Microarrays of 4, 16 and 36 thermally-isolated and individually-addressable microhotplate elements are used. Each ~ 100 μm x 100 μm element can rapidly measure and control temperature (20 °C to 500 °C) locally, and also monitor the electrical properties of deposited films using surface microelectrodes. The primary advantage of the approach is that a large number of different sensing films can be fabricated and screened for sensing properties in one experiment and in a very small area.



SEM images from a 16-element array in which $TiO_2$ was grown by CVD with each element held at a different temperature. All images are at the same magnification.

We have demonstrated this approach for the CVD growth of $TiO_2$ (from titanium nitrate - see figure - and titanium isopropoxide) and $SnO_2$ (from tin nitrate) sensing films. The microarrays enable highly efficient database development to correlate film processing and sensing performance. The multi-sample studies on $TiO_2$ and $SnO_2$ have proven extremely valuable in identifying deposition protocols for sensing films that perform well in a DTRA-sponsored project for chemical warfare agent detection, and in a NASA-sponsored project for detecting trace gases in planetary environments. We have also

examined the thermal processing of high area porous $SiO_2$ structures from silsesquioxane-block copolymer blends for fabricating microscale preconcentrators.

**Impact:** We have demonstrated that combinatorial microarray platforms can be used to accelerate the development of chemically functional materials for chemical sensing. The MEMS-based platforms are expected to be broadly applicable to other materials science research problems.

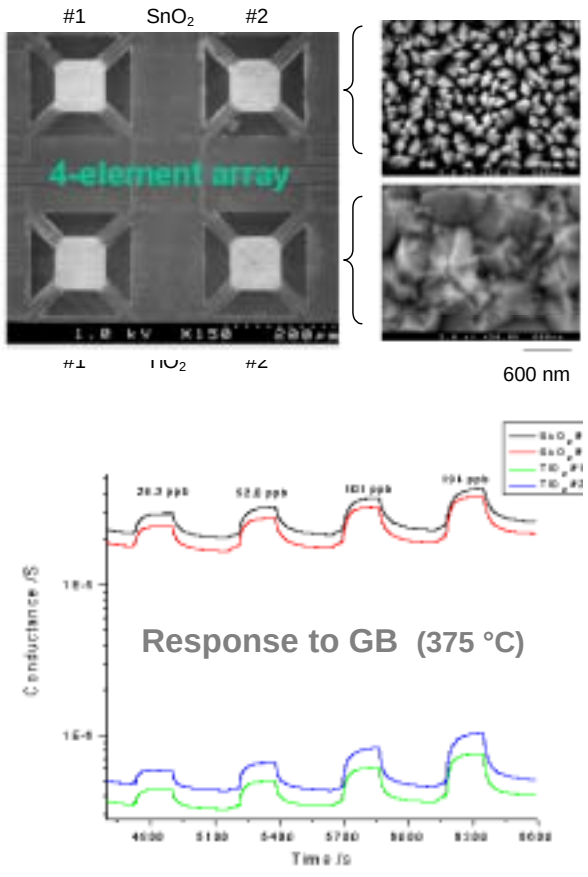
**Future Plans:** Using the same strategy we plan to examine the deposition of novel nanomaterials, such as carbon nanotubes, thin-walled oxide networks, and nanowires, that hold great promise for chemical sensing applications.

# Chemical Warfare Agent Detection with Microsensor Arrays

**CSTL Program**: Industrial and Analytical Instruments and Services
**Authors:** *C.J. Taylor, R.E. Cavicchi, D.C. Meier, and S. Semancik*

**Abstract**: MEMS-based microsensors were used to detect chemical warfare agents in a project supported by the Defense Threat Reduction Agency (DTRA). The microsensors are based on surface-micromachined 100 µm x 100 µm platforms called microhotplates. The agents are detected by measuring conductance changes in metal oxide thin films deposited on the microhotplates; the sensor response is correlated with the identity and concentration of chemical agent present. Microsensors are tuned for specific agents by incorporating metal oxide films of different composition into arrays of sensors, and by selecting different fixed and time-varying temperature programs. Studies were first conducted on simulant agents at NIST to develop appropriate device prototypes for testing the technology on actual sulfur mustard and nerve agents at a surety laboratory. Sensor array sensitivity, reproducibility, and stability measured in the chemical warfare agent tests are encouraging.

**Technical Highlight:** Studies done at NIST and a surety laboratory have established that conductometric microsensors based on oxide sensing films and temperature-controllable MEMS platforms can detect a variety of chemical warfare agents. These types of microsensors may some day be used to warn military personnel and civilians of releases of chemical warfare agents. As part of the work, the sensing performance of 4-element microsensor arrays to the simulant molecules of chloroethyl ethyl sulfide (CEES) - a sulfur mustard simulant, and diisopropyl fluorophosphates (DFP) - a nerve agent simulant, was also evaluated. The simulant experiments were performed to develop sensing materials and operating schemes suited to the classes of compounds used in chemical warfare. The first phase of testing on three agents, sulfur mustard gas (HD) and the nerve agents tabun (GA) and sarin (GB) was completed in experiments conducted at the Edgewood Chemical Biological Center (ECBC).




Nano-crystalline tin and titanium oxide sensing films on in a 4 element microhotplate array with conductance response.

Microsensor response signals were generated as changes in resistance (conductance) of thin $SnO_2$ and $TiO_2$ films as they were exposed to the agents. The nanocrystalline sensing films were fabricated on microhotplate platforms by chemical vapor deposition, and operated between 20 °C and 480 °C in both fixed- and variable-temperature modes. These tests demonstrated that the devices can detect the agents in the 0.01 to 0.3 ppm range with adequate signal-to-noise. Good stability and reproducibility were observed

over 14-hour continuous monitoring runs. Since "LC50" concentration levels for 10-minute exposures are ~ 1 ppm for the agents tested, it is clear that the microsensors are sensitive enough for a practical monitoring technology.

**Impact:** The NIST microsensor technology offers other desirable features for agent detection including low power consumption, low cost, ease of including redundant devices, and ability to readily integrate on-board electronics for signal conditioning.

**Future Plans**: Efforts will determine the ability to distinguish between agents and common interferences such as water, fuels, and pesticides. In addition, mathematical data processing methods will be evaluated for enhancing the recognition and quantification of agent signals, while suppressing that of interferences. We will also explore new sensing materials and expand our test set to include an additional agent class.

# Error Free Liquid Flow Diverters for Calibration Facilities

**CSTL Program**: Industrial and Analytical Instruments and Services
**Authors:** *T.T. Yeh, and P.I. Espina (836); and N.P. Yende (CSIR-National Metrology Laboratory)*

**Abstract:** As NIST has refurbished its water flow rate measurement facilities, research on methods to reduce this gravimetrically-based system's measurement uncertainty. Diversion of the flow passing through metering devices into the system's collection tank is a operation critical in accurate measurement of the flow rate. Various techniques have been suggested to reduce diverter valve errors in commonly used valve structures. A new concept has been developed that makes use of a double-action flow diversion process whereby the components of the diverter valve error are self-canceling. This self-cancellation effect occurs when the flow accumulation for the first and second diverter valve sweeps are functional inversions, summing to the full calibration flow at corresponding times in their diversion period. Several variations in the general approach have been developed conceptually and one of these options has been chosen for testing and implementation. Initial testing indicates substantial reduction in diverter error component contribution.

**Purpose:** Improve national liquid flow measurement standards and methods to support improved accuracy in their dissemination.

**Major Accomplishment**: Flow diverter valves are important components in most liquid flow calibration systems, functioning to direct the flow to either a bypass loop or a collection tank. Figure 1 shows a sketch of a typical time history of a flow diverted into a collecting tank during a calibration cycle. During a typical calibration cycle, the flow diverter valve makes two sweeps through its trajectory. During the first sweep, the flow is diverted from the bypass loop into the collection tank. The collection tank then accumulates liquid, followed by a second diverter valve sweep, which redirects the flow to the bypass loop. During the diverter valve sweeps, the flow into the collection tank changes from zero to the full flow and from full flow to zero. Since only a fraction of the full calibration flow enters the collection tank during a diverter valve sweep, diverter valve errors are manifested as an uncertainty in the liquid collection time. These errors can contribute significantly to flow measurement uncertainty in static weighing techniques and are often the dominant uncertainty component.

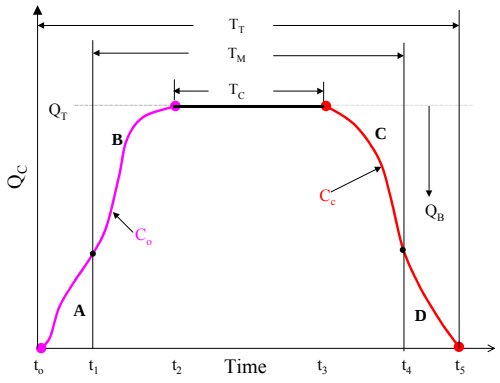



**Figure 1.** Liquid flow collected as function of time. For clarity, the constant collecting flow interval, $T_c$, has been compressed

Traditionally, designing fast actuation flow diverter valves and using symmetric time actuation has reduced uncertainty associated with liquid collection time. In practice, symmetric time actuation is realized by locating the time triggering signal at the diverter valve mid-trajectory point. However, the desired error reduction is only assured when both the valve's liquid jet velocity profile and the diverter velocity are symmetric. In practice, these conditions are difficult to obtain across the entire flow range of a calibration facility, resulting in diverter valve errors over most of the flow range.

Various techniques have been suggested to reduce diverter valve errors. In one technique, the diverter valve error is amplified by making repetitive liquid collections which, when totaled and compared to a single diversion, permit evaluation of the error. Another method for determining the diverter valve error uses successive measurements of flow rate at different collection times. The results of these collections are fitted to estimate the timing error. CFD designs of the feeding pipe and nozzle geometry have also been used to try to achieve symmetric jet velocity profiles, thereby reducing diverter valve error.

In an effort to reduce the uncertainty for calibration facilities, we have introduced a diverter valve design that eliminates error even when symmetrical conditions are not satisfied. This new concept makes use of a double-action flow diversion process whereby the components of the diverter valve error are self-canceling. This self-cancellation effect occurs when the flow accumulation for the first and second diverter valve sweeps are functional inversions, summing to the full calibration flow at corresponding times in their diversion period. The proposed diverter valve design achieves the self-cancellation effect by implementing repeated unidirectional diverter motion, which has an identical time actuation during both sweeps. The unidirectional motion of this design contrasts with conventional designs where the diverter moves in opposite directions during the two sweeps. The advantage of the proposed design is that, theoretically, it eliminates the diverter valve error for any liquid jet velocity profile.

Several operational examples with different liquid jet velocity profiles and diverter speeds have been examined theoretically to show the diverter characteristics for each. Several design options and their operational procedures were also considered. An experimental test of the performance of a selected new diverter is currently underway. If successful this diverter valve design will be incorporated into our waterflow calibration facility, which is currently being refurbished.

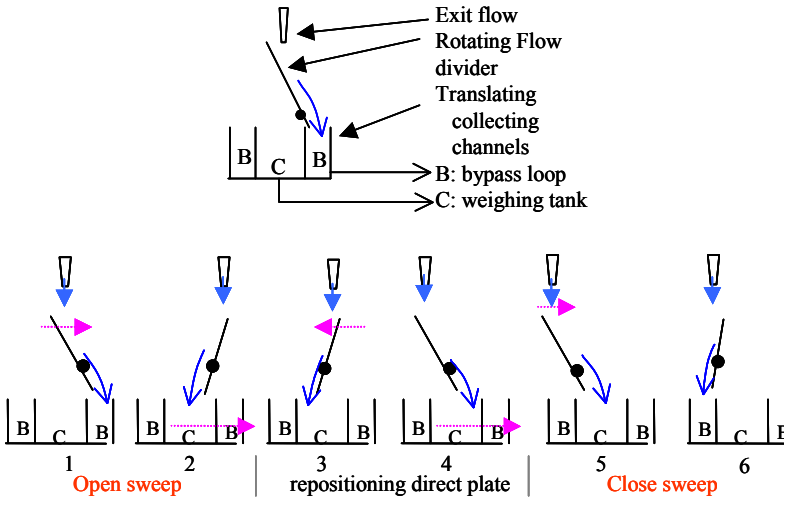



**Figure 2**. A rotating diverter valve with translating flow-directing channels

**Impact:** Reduced measurement uncertainty in liquid flows provides U.S. industry with improved accuracies and maintains U.S. leadership in flow rate metrology globally.

**Future Plans:** Complete evaluation of this approach in ~50 mm pipe sizes to quantify uncertainty component contributions. If reduction in component uncertainty is significant, incorporate this design in the refurbishment of the main water flow rate measurement facilities at NIST.

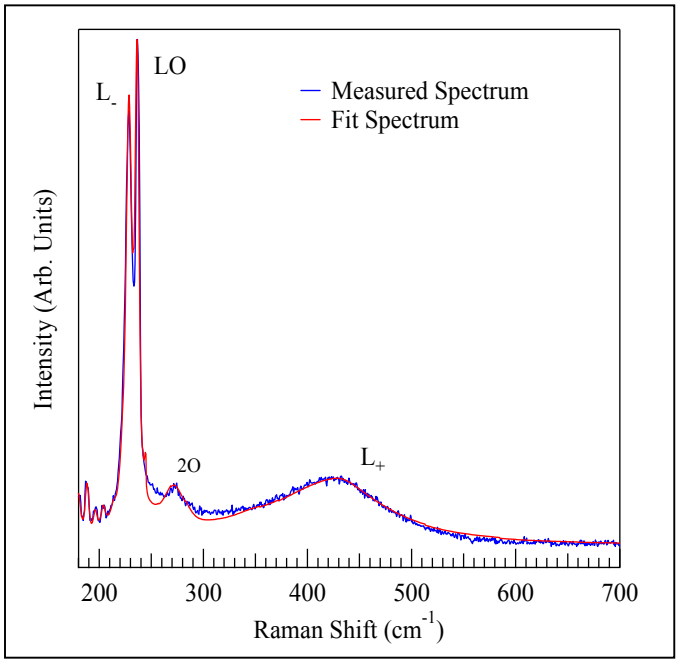
# Non-Contact Free Carrier Density Measurements for Compound Semiconductors

**CSTL Program**: Microelectronics
**Authors:** *J.E. Maslar, and W.S. Hurst*

**Abstract:** Transport of free carriers is central to the operation of all optoelectronic devices and reliable measurement of the carrier properties is critical. Hall or capacitance-voltage measurements are traditionally used to obtain this information, but require electrical contact. This precludes their use *in situ* during growth or processing and, typically, even on actual device layers. Raman spectroscopy, as an optical technique that can be used for transport property determination, does not suffer from these limitations. In addition, it is non-destructive, spatially resolved, and can be applied to a specific buried layer, sometimes a problem for traditional electrical measurements. A number of issues exist that are central to determining the accuracy and precision of this method, including the semiconductor under investigation, measurement system parameters, and Raman spectral model used to fit the measured spectra. NIST is systematically addressing such issues. The results of this investigation should facilitate the utilization of Raman spectroscopy for spatially resolved off-line characterization, as well as process monitoring and control during film growth and etch processing.

**Purpose:** Facilitate the development of a non-contact, spatially-resolved measurement of majority carrier concentration and mobility in compound semiconductors by establishing the accuracy and precision of Raman spectroscopy for a given material, set of measurement conditions, and Raman spectral model.

**Major Accomplishments:** Raman spectroscopic systems, optimized for narrow and wide band gap materials, were assembled and used to measure the Raman spectra of n-type doped GaN, GaAs, and GaSb films. An example of the measured Raman spectrum for n-type GaSb is given in the figure. Fitting the data with a Raman spectral model results in a determination of carrier concentration of ~6 x $10^{18}$ $cm^{-3}$. Relatively simple spectra models were developed and employed to determine free carrier concentrations from the experimental Raman spectra.




**Impact:** This project facilitates the utilization of Raman spectroscopy for spatially resolved off-line characterization, as well as process monitoring and control, during film growth and etch processing. A potential user should be able to determine the expected accuracy and precision for a given material, set of measurement conditions, and Raman spectral model.

**Future Plans:** To develop more sophisticated spectral models in collaboration with Divisions 812 and 842, and to extend measurements to p-type doped films and alloy semiconductors, e.g., AlGaAs and AlGaN.

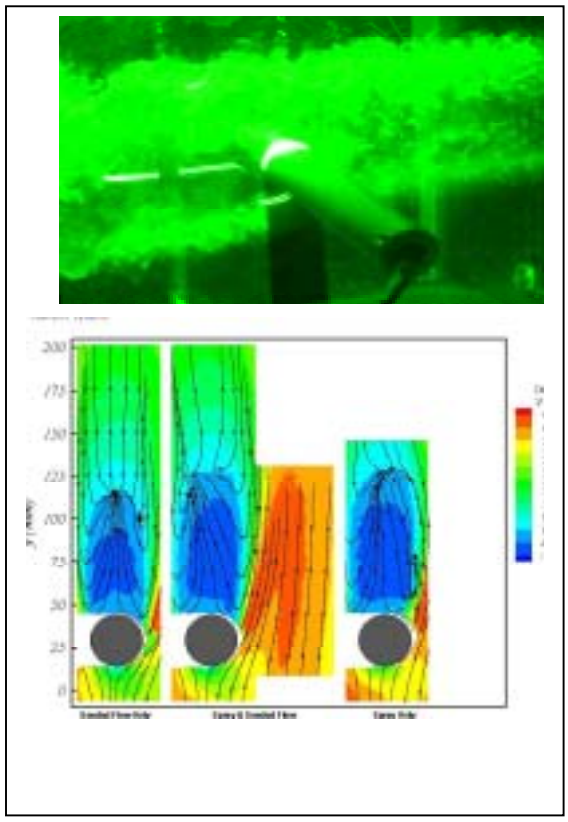
# Benchmark Data on Liquid Fire Suppressants

**CSTL Program:** Automotive and Aerospace
**Authors:** *C. Presser (836); J.D. Widmann (866); G. Papadopoulos (Dantec Dynamics); and P. DesJardin (Sandia National Laboratory)*

**Abstract:** The new generation of non-ozone-depleting Halon alternatives include chemical suppressants that have high boiling point temperatures (i.e., Tb > 330 K) and exist in liquid phase under high-pressure release or in ambient conditions. Release of these agents in a confined cluttered space, results in the dispersal of droplets that either travel along ballistic trajectories, move with the convecting flow, or impact nearby solid obstacles. Therefore, an accurate representation of agent droplet transport is crucial for the numerical modeling of fire suppression in confined spaces. To better understand the physics of droplet transport around and behind solid objects, an experiment where controlled grid-generated turbulence was imposed on the air stream. Experimental results provide new data for a well-characterized, homogenous droplet-laden turbulent flow field around prescribed obstacles (top Figure). Results are obtained using particle image velocimetry, phase Doppler interferometry, and visualization techniques. The liquid agents considered in the investigation were water, and two 3M$^{TM}$ fire protection fluorocarbons HFE-7100 (with a boiling point of 334 K) and HFE-7000 (with a boiling point of 307 K).

**Purpose:** Develop a parametric data set to guide and validate the Vulcan fire modeling efforts underway at Sandia National Laboratory.

**Major Accomplishments:** Particle image velocimetry (PIV) experiments were completed with the assistance of Dantec Dynamics to characterize the impingement and transport of a water spray around a cylinder and body-centered cube arrangement of spheres that represents a more complicate obstacle. Measurements upstream and downstream of a 33 mm cylinder having a 250 W heater and thermocouples to monitor the near surface temperature(see bottom figure) were completed. The cylinder was heated to 423 K to study the effects of a heated surface on droplet vaporization and transport, as a droplet approaches the heated surface. The results indicated that the transport of droplets around the cylinder is highly dependant on droplet size, and spray impingement and surface wetting caused significant cooling of the heated surface.



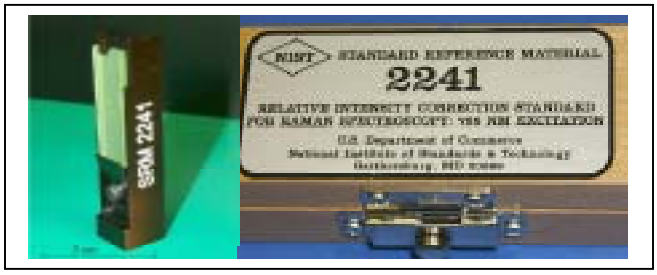
**Impact:** Establish correlation of the agent/spray properties, agent atomization methods, and agent dispersion effectiveness that will enable (in fire modeling and scale-up to intermediate- and full-scale testing) optimization of fire suppression performance of misted liquid systems.

**Future Plans:** Plans are underway to initiate measurements with the phase Doppler interferometry system and to obtain spatial profiles of the droplet size and velocity distributions, and droplet number density upstream and downstream of the obstacles for water, HFE-7100 (with a boiling point of 334 K), and HFE-7000 (with a boiling point of 307 K).

# Standards for Raman Spectroscopy

**CSTL Program:** Industrial and Analytical Instruments and Services
**Authors:** *W.S. Hurst, and S.J. Choquette (839); E.S. Etz (837); and J. Maslar (836)*

**Abstract:** Raman spectroscopy is now finding its place in the industrial environment for process measurements and quality control. The lack of accepted practices, standards and spectral libraries has been a main obstacle to the acceptance of Raman in industrial settings and is a barrier to its use in the regulated industries. This project critically evaluates existing approaches and develops new methods and associated standards that will provide for calibration of the intensity of Raman spectral data. Intensity calibration is needed to make process-control Raman measurements instrument independent for analysis of unknown mixtures, and for reliable and robust quantification. NIST is developing a series of fluorescent glasses that will become available as Standard Reference Materials, and provide instrument calibration. SRM 2241, a glass suitable for use with laser excitation at 785 nm, has been fully characterized and made available this year. A new fluorescent glass with stable properties suitable for use with laser excitation at 532 nm has been developed and is in the final stages of measurement and analysis for use as an SRM.




**Purpose:** Intensity calibration of Raman spectra can be accomplished using white light sources, but this procedure requires expensive equipment, has a source with a limited lifetime, and provides a radiation source that is spatially different from the Raman process. These limitations can be avoided by using fluorescent glass artifacts of known relative irradiance. NIST will develop glasses for intensity calibration for use with popular laser excitation wavelengths that will be available as a set of Standard Reference Materials (SRMs) traceable to NIST primary radiometric standards.

**Major Accomplishments:** A chromium-oxide bearing glass with broadband fluorescent radiation suitable for use with 785 nm laser excitation has been developed and characterized using three different commercial Raman spectrometers. It has been issued as SRM 2241, which supplies the glass artifact along with a curve expressing its relative irradiance as a function of the Raman shift in wavenumbers ($cm^{-1}$). A new fluorophore and glass matrix composition for use with 532 nm excitation has been developed. This glass is stable, completely resistant to laser bleaching, and has adequate broadband spectral response. It is in the final stages of characterization and therefore should be available as SRM 2242 in mid-FY03.

**Impact:** This program is providing industry with an inexpensive and easy means for calibration of the Raman spectral intensity. This will promote the acceptance of the relatively new use of Raman spectroscopy in industry and provide a means for instrument qualification as required by regulatory agencies.

**Future Plans:** Complete work on SRM 2242 as an intensity standard for excitation at 532 nm. Develop a glass suitable for use at 488 nm and 532 nm and made available as SRM 2243 in FY03. Initiate preliminary work on a glass for use with FT-Raman at 1064 nm that will be available as SRM 2244. Also develop a doped-glass system with usable properties for use at 633 (and possibly 647 nm) to be made available as SRM 2245.