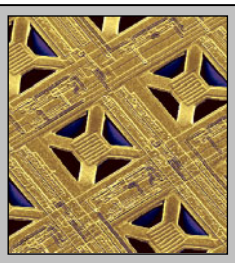
Process Measurements Division -Table of Contents

Process Measurements Division
James R. Whetstone, Chief



Process Measurements

J. Whetstone, Chief

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

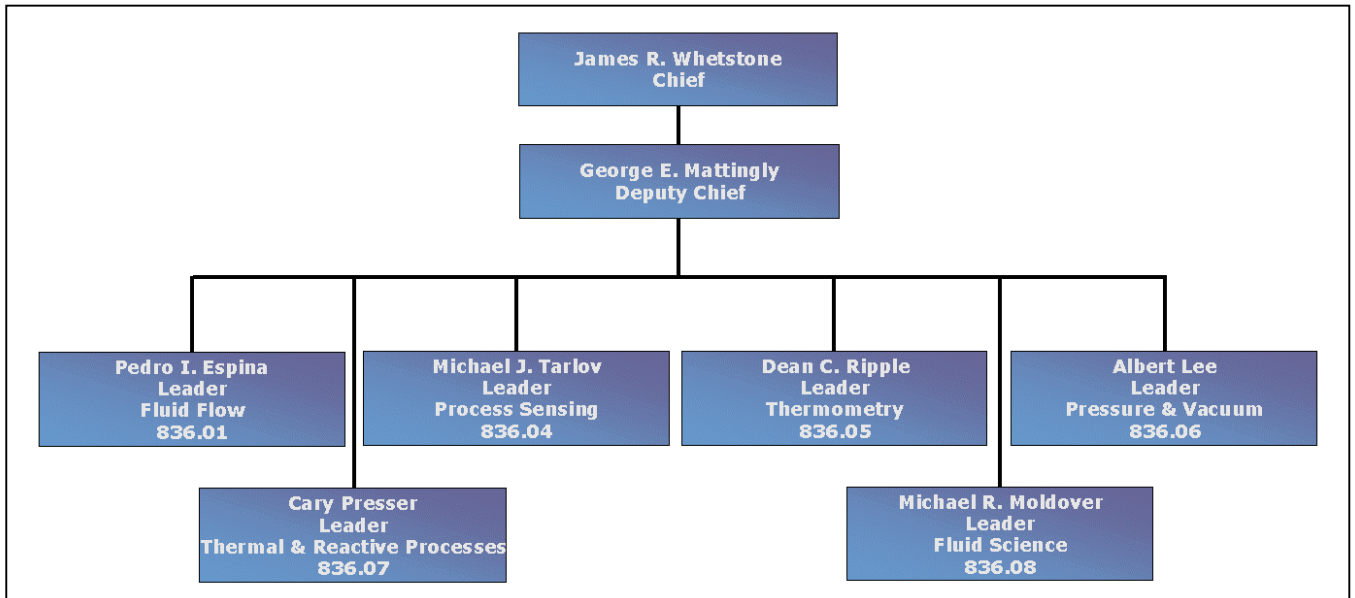
Division Overview

Mission:

The Process Measurements Division develops and maintains technical competencies and capabilities in support of CSTL programs. The Division pursues research efforts in measurement science as the basis to enhance measurement standards and services, measurement techniques, recommended practices, sensing technology, instrumentation, and mathematical models required for analysis, control, and optimization of industrial processes. Improvement and dissemination of national measurement standards for temperature, fluid flow, air speed, pressure and vacuum, humidity, liquid density and volumetric measurements are core Division responsibilities. The Division's research seeks fundamental understanding of, and generates key data pertinent to, chemical process technology. These efforts include the development and validation of data-predictive computational tools and correlations, computer simulations of processing operations, and provision of requisite chemical, physical, physical property, and engineering data.

Organizational Structure:

The Division, which contains the equivalent of 71 full-time staff members representing a range of technical competencies and including 4 NIST/NRC Post Doctoral Fellows. Additionally, the Division hosted 8Guest Researchers from academia, industry, or sister National Measurement Institute and utilized the expertise and skills of 18 contractors. The Process Measurements Division is comprised of six groups with the mission statements given in the following. Our efforts support six of the 12 CSTL program areas. The organization of the Division supports the evolution and strengthening of competencies necessary for program success.



Organizational Chart
Process Measurements Division
Chemical Science and Technology Laboratory

Process Measurements Division Activities
In Support of CSTL Program Directions in:

Semiconductor Metrology **Nanotechnology** **Process Metrology**
Physical Property Data **Chemical and Biochemical Sensing** **Chemical and Biochemical Data,**
International Measurement Standards

Competency Areas

Fluid Mechanics	Flow Measurements	Computation Fluid Dynamics
Chemical Process Modeling	Spray Systems	Optical Particle Characterization and Sizing
Thermometry	Humidity Measurements and Stnds	
Piston Gauges and Manometry	Vacuum Measurements and Stnds	Raman Spectroscopies
Laser Diagnostic Techniques	Surface Plasmon Resonance	Spectroscopy Absorption Spectroscopies
Cavity Ring Down Spectroscopy	Plasma Diagnostic Techniques	MEMS & Solid State Chemical Sensing
Microfluidic Devices	Acoustic Measurements	Physical Properties of Fluids

Fluid Flow Group

- Establish, maintain, and disseminate the reference standards needed by U.S. industry for fluid flow rate and liquid quantity measurements,
- Conduct research to advance fluid transfer measurement science,
- Establish and maintain international comparability in fluid flow rate and fluid quantity measurements, and
- Interact with industrial counterparts and standards committees to provide expertise and assistance to U.S. industry and other government agencies in advancing fluid transfer technology.

Process Sensing Group

- Develop, validate, and apply state-of-the-art measurement techniques and sensors for process optimization and control of plasma reactors used in semiconductor manufacturing,
- Develop scientific and technological under-pinning for application-tunable, low-cost, micro-machined gas sensor arrays to meet measurement needs in process control, emissions monitoring, and hazardous gas detection, and
- Provide scientific and technological foundation for the use of ultrathin organic films in sensing and diagnostic applications in chemical and biochemical process monitoring and health care.

Thermometry Group

- Realize, maintain, and disseminate the national standards for:
    - temperature, (the International Temperature Scale of 1990, over the range 0.65 K to 1235 K) and
    - humidity, (moisture in air: 5 nmol/mol to 75 mmol/mol),
- Perform research on developing or improving primary standards and measurements for temperature and humidity,

- Develop methods and devices to assist user groups in the assessment and enhancement of the accuracy of their measurements of temperature and humidity, and
- Co-ordinate and participate in international comparisons of realizations of the International Temperature Scale of 1990 and of national standards of humidity.

Pressure and Vacuum Group

- Develop and maintain primary pressure, vacuum, and low gas flow standards and disseminate the measurement capability to U.S. industry,
- Advance pressure, vacuum, and low gas flow measurement science:
    - Conduct research to develop measurement standards and techniques to meet U. S. industry requirements,
    - Perform benchmark measurements of material properties and investigate fundamental physics of industrially important phenomena which require state-of-the-art pressure, vacuum, and low flow measurements, and
    - Collaborate with industry and academia in the development of new instrumentation to improve industrial process control or for use in critical scientific measurements.

Thermal and Reactive Processes Group

Develop advanced mathematical models, advanced measurement techniques, standard measurement practices and performance data for analysis, control, standardization, and optimization of key industrial processes; current focus is on:

- liquid atomization and spray combustion, and
- chemical vapor deposition.

Fluid Science Group

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

Programs:

The Division pursues measurement science research and development projects and measurement standards dissemination activities that contribute to accomplishing CSTL programs. In several cases the breadth of potential applications of our research work is such that project results impact several CSTL program areas. Brief description of our activities follow. Summaries of FY 2000 program accomplishments are given in the 23 technical articles that follow this overview.

Semiconductor Metrology

CSTL's Semiconductor Metrology program contributes to the NIST National Semiconductor Metrology Program (NSMP) that is managed by the Office of Microelectronic Programs (OMP) of the NIST Electrical and Electronic Laboratory. CSTL competencies in several areas contribute to metrology developments need 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 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 transfer 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,
- models for contamination control in thermal CVD processes,
- methods to determine electrical, physical, and chemical properties of plasmas used for etching and reaction chamber cleaning processes, and
- very low-level water vapor measurements and standards 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) National Technology Roadmap for Semiconductors (ITRS). In fact, modeling is specifically identified not only as a "crosscutting technology," but as "pervading all crosscuts." Our program in this area, partially supported by the NSMP, seeks to develop and validate benchmark chemical mechanisms and supporting thermochemical and kinetic data, for equipment and process design and control.

Program Highlights

Many of the processes used in semiconductor manufacturing are inherently chemical in nature. The reactants are introduced in the gas phase resulting in the wide use mass flow controllers (MFCs) to meter the appropriate quantity of material to the reaction vessel. Division efforts are directed toward improving both the flow standards used in industry for **MFC calibration and thermophysical property data** for a range of process gases. MFCs are normally calibrated with

benign surrogate gases, e.g., N_2, CF_4, SF_6, and C_2F_6, but are then are used to deliver reactive process gases, e.g., Cl_2, HBr, BCl_3, WF_6, using 'gas factors' to adjust for gas property differences. Application of 'gas factors' to MFC calibrations often thought to be the source of significant errors in the quantity of gas delivered to the process. In FY 2001 experimental results for additional gases were made available on the website, http://www.properties.nist.gov. In addition a prototype low flow rate transfer standard was developed and used for provisional evaluation of in-house standards used by one MFC manufacturer.
The semiconductor manufacturing industry needs higher accuracy than currently available in measuring the temperature of silicon wafers during **Rapid Thermal Processing** to achieve goals in product quality and device performance. Consequently, the industry roadmap now requires an uncertainty of ≤ 2 °C at 1000 °C for RTP for the next generation of wafer patterning. Radiation thermometers are used in RTP but the uncertainty in measurements made with them is unacceptably large when the thermometers are calibrated against blackbodies.

We are developing improved calibration techniques for the light-pipe radiation thermometers (LPRTs) used to control RTP systems. Si wafers instrumented with combinations of stable thin-film and Pt/Pd wire thermocouples (TCs) minimize errors from heat transfer that would be present for other types of temperature sensors. In FY 2000 we increased the operating temperature of our TC-instrumented calibration wafers to 1000 °C to meet the upper temperature requirement seen in industrial operation while continuing to improve our understanding of sources of measurement uncertainty. Additionally, we have investigated the effect of the operating temperature of the light pipe portion of the LPRT on the indicated temperature and have found that the radiation surroundings can have significantly effects.

Our technology transfer activities have continued and expanded. Our cooperative project with SEMATECH, University of Texas, and Sensarray Inc. has included both the design, fabrication, testing, calibration, and delivery of two thin-film calibration wafers for testing in their unique RTP instrumentation test bed. Other industrial and academic technical transfer activities have included providing thin-film calibration wafers to Applied Materials and Vortek Industries for test and evaluation in commercial RTP tools. Additionally, the NIST patent on the "Temperature calibration wafer for rapid thermal processing using thin-film thermocouple" #6,037,645 was issued Mar. 14, 2000 and licensed to Watlow Gordon Inc. for commercial production of the thin-film/wire thermocouple instrumented wafer technology.

Particle formation from gas phase reactants in CVD reactors is a contamination source not well described by **CVD process simulation models** due to inadequate of particle formation mechanisms in these complex systems. The Division is developing models describing silicon deposition that include gas-phase nucleation, condensation, and growth of particles in a rotating disk CVD reactor. Particle scattering intensities were measured experimentally via laser light scattering and were compared with those predicted by the semi-empirical NIST microcontamination model and found to be in close agreement. This model contains two empirical parameters relating thermophoretic force and condensational sticking coefficient. Proper choice of these parameters results in the excellent agreement between experimental results and model prediction. In the coming year we will extend the modeling effort to a more physically based particle formation mechanism, determine gas phase concentrations near the particle layer, and begin looking at the effects of dopant gas influence on the system.

Our research activities in this program is described in Technical Reports 1 – 6.

Process Metrology

The Division contributes substantially to the CSTL Process Metrology Program. Our efforts include a broad range of research activities. A significant portion of these efforts maintains and advances national measurement standards for temperature, fluid flow, air speed, pressure and vacuum, humidity, liquid density and volumetric measurements. Several of our measurement science research projects address the development and demonstration of new approaches to the realization and effective dissemination of national measurement standards. The thrust of these efforts is the reduction of measurement uncertainty in the realization of national measurement standards. The expertise resulting form these efforts directly supports CSTL's International Measurement Standards Program in which U.S. national standards are compared with those maintained by other National Metrology Institutes (NMIs). The Division is responsible for all physical measurement standards provided by CSTL. Dissemination of and access to these national measurement standards is accomplished through our instrument calibration services. Therefore, several activities involve enhancing and disseminating national measurement standards to industry and other government agencies.

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

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

The Division's efforts supporting CSTL's Process Metrology Program include:

- advances in flow measurement standards and new approaches to flow measurement methods,
- development of standard for low concentrations of water vapor in gases,
- high sensitivity optical detection methods based on evanescent wave cavity ring down spectroscopy,
- improving the accuracy of thermodynamic temperature measurements,
- standards for Raman spectroscopy,
- a new approach to primary pressure standards based on toroidal cross capacitors and high accuracy electrical measurements, and
- improvement in piston gauge pressure standards.

<u>Program Highlights</u>

We continue to improve **pressure measurement standards** both through advances in the more traditional piston gauge technology and through the development of new approaches to absolute

pressure measurement. Piston gauge uncertainties are described by the uncertainty in their effective area. Recent advances in manufacturing technologies have reduced dimensional tolerances of pistons and cylinders the sub-micron level providing the opportunity to accurately dimension these components with nanometer resolution. We have taken advantage of a newly commissioned dimensioning system at the German national metrology institute, *Physikalisch-Technische Bundesanstalt*, which currently has the smallest measurement uncertainty of an NMI in these types of dimensional measurements. We sent our piston and cylinder components there for comprehensive dimensional determinations of. The roundness and straightness measurements obtained from PTB were compiled to form a three-dimensional grid structure and resulted in a relative uncertainty of the area of between three and four ppm at 20°C and at zero applied pressure. In FY2001, we plan extensive testing to quantify all uncertainty components and comparison the gauge with the ultrasonic interferometer manometer as well as with other reference piston gauges. In addition, the thermal expansion and pressure coefficients of the gauge will be quantified. We anticipate a reduction in the uncertainty of approximately four times that of our currently stated value. These developments may represent the ultimate precision obtainable with this technology.

An alternative approach to pressure standards continues through the measurement and calculation from first principles the dielectric constant of helium, $\varepsilon(p)$, with sufficient accuracy to make the pressure uncertainty obtained from existing standards (piston gages) significantly larger than the pressure uncertainty obtained from in $\varepsilon(p,T)$. Dielectric constant measurements are being improved by drawing on NIST's expertise in electrical metrology. With that expertise a novel, doughnut-shaped, four-electrode cross capacitor has been developed. For helium pressures up to 7 MPa, the cross capacitor concept was experimentally proven at the level of approximately $0.3\times10^{-6}\times\varepsilon(p)$. Further development of this approach may result in the ability to measure pressure at level approximately one of order of magnitude below our current capability. In addition to investigation as a potential pressure standard, the cross-capacitor system has been used to make reference-quality measurements of ε(p) for methane, nitrogen, carbon dioxide, argon, and helium at 50°C. This work also supports CSTL Chemical and Biochemical Data program.

Our research in this program is described in the Technical Reports 7 – 16.

Chemical and Biochemical Sensing

The Division has a significant effort supporting the CSTL Chemical and Biochemical Sensing Program with two research activities: micro-machined gas sensor arrays and diagnostic applications of self-assembled monolayers (SAMs). Chemical sensor research is collaborative with the Semiconductor Electronics Division of the Electronics and Electrical Engineering Laboratory. The technology is based on NIST developed, and patented, 'micro-hotplate' arrays formed by silicon micro-machining. Chemical sensors are fabricated by depositing metal oxides, e.g., SnO_2, and surface-dispersed catalytic metal-additives on the micro-hotplate to form robust, electrical-conductance-based sensing elements. The objectives of our effort are to develop the knowledge base required to optimize multi-species detection and quantitative analysis and to resolve generic device-processing issues that could limit commercial application. In FY 2000 we developed methods that significantly increase the sensitivity and stability of micro-hotplate chemical sensors. Sensitivity to methanol in air at the 10 ng/g level were demonstrated using a nanoparticle-

based sensing material. In addition stable performance of the device was demonstrated over a 100-hour testing period. Also, nanophase, doped sensing oxides produce high sensitivities without the fouling effects that are often observed on metal catalyst-doped films. Technical Report 18 discusses these developments.

The second activity investigates alkanethiol monolayers, of the general formula $X(CH_2)_nSH$, self-assembled on the surfaces of noble metal substrates. These SAMs are robust, reproducibly prepared structures with highly tunable surface properties, and serve as a model system for the study of many sensing applications. An example is DNA microchip technology, which has potential application in the areas of disease detection, toxicology, forensics, industrial processing, and environmental monitoring. Our research currently is focused on the self-assembly of DNA monolayer films on surfaces and on their use as DNA probes. We have demonstrated the dependence of hybridization efficiency on target length and developed methods to develop near defect-free SAMs. These developments are discussed in Technical Report 19.

Chemical and Biochemical Data

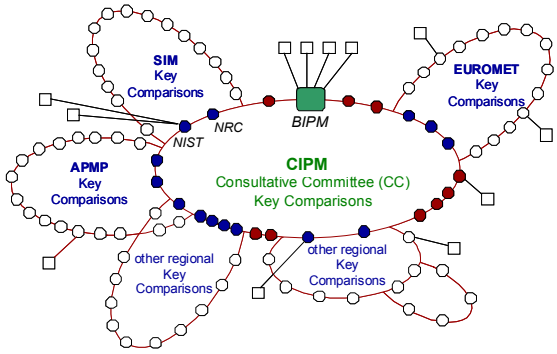
Division efforts in the Chemical and Biochemical program focus on development of benchmark experimental data for input and validation of multiphase combustion models in addition to development of methods for calibration of instruments and sensors and advanced diagnostic techniques. Computational Fluid Dynamic modeling is widely used by to design and optimize industrial combustion processes and systems. Although modeling can be cost-effective design tool, model validation is critical to success. In spray combustion data droplet field characteristics, flame structure, heat transfer, and particulate/gaseous reaction products and the interrelation with operating conditions are critical to the accuracy of a models predictive capabilities. This year a benchmark experimental database was released to our partners in industry and academia. A one-day workshop was held to further identify future needs for multiphase combustion data. A primary concern of both industry and the regulatory community is the issue of particulate matter entering the environment. The need for particulate matter standards was identified as a high priority area where NIST could make a significant impact. Technical report 20 discuss this topic is greater detail.

Nanotechnology

The Division contributes to CSTL's Nanotechnology Program in the micro-fluidic device technology area. This research is focussed on dynamic behavior, chemical selectivity, and detection in micro-channel structures and is collaborative with the Analytical Chemistry Division. Although micro-fluidic, or so-called "lab-on-a-chip", devices are currently receiving considerable attention and successful miniaturization of a broad range of chemical analysis techniques is impeded by poorly understood mechanisms that control their operation. Research efforts in this NIST competence project investigate the behavior of micro-channel structures formed in polymer substrates. Although miniaturized devices for DNA sequencing have recently become available commercially, the high cost of silicon-based devices will limit applications to a limited number of areas. Realization of the potential of micro-fluidic devices requires that manufacturing cost be significantly reduced. Polymer-based structures have this potential, but also present a number of challenges to their successful use. Although, micro-channels are easily formed in polymers, the movement of fluid through them reliably is still problematic, particularly using electro-osmotic flow (EOF) methods. EOF is simple and widely used but is adversely affected by

micro-channel surface properties in these large surface-to-volume ratio structures. We have measured electroosmotic mobility and flow profiles in different plastic devices and developed methods of treating micro-channel surfaces in different plastics to provide device designers with greater operational reliability. Such fundamental data relating flow to surface properties will enable developers of this technology to tailor plastic microfluid channels for specific applications.

Comparison Scheme for Key Comparisons agreed under the MRA



International Measurement Standards

As the National Measurement Institute of the U.S., NIST is responsible for comparison of U.S. national measurement standards with those of other nations. Such comparison efforts are performed under the auspices of the Committee International des Poids et Mesures (CIPM) and its various consultative committees. In addition, coordination of similar efforts with Regional Metrology Organization such as Sistemo Interamericano Metrologia (SIM) which includes the countries in the Americas are designed to extend the comparison efforts to as many participants as practicable.

Standards comparisons activities among NMIs are organized by the the respective Consultative Committees of the CIPM and initiated in selected NMIs which are then designated Pilot Laboratories. These Pilot Laboratories design and pre-test the transfer standards and test procedures; they arrange and schedule tests among participating NMIs; and they analyze data and report results.

In FY 2000 our efforts in this program have continue at a somewhat reduced level from previous years due to the completion of several activities. The following is a brief summary of these efforts.

Comparisons of realizations of the International Temperature Scale of 1990 (ITS-90).

The Division is participating in four Key Comparisons (KC) of realizations of the ITS-90 organized by the CIPM Consultative Committee for Temperature (CCT). We are the pilot laboratory for KC 3 [83.8058 K (Ar triple point (TP)) to 933.473 K (Al freezing point (FP))] with 14 national laboratories plus Bureau International des Poids et Mesures (BIPM) participating. The measurements phase of the work has been completed and this year an exhaustive report has been written. The report will be finalized and submitted to the CCT for its acceptance in early FY 2001. Efforts in the remaining 3 Key Comparisons continues.

Expansion of KC3 with SIM is under discussion with interested NMIs of the Americas. NIST involvement in developing the procedures and protocols for this comparison is currently in the discussion phase due to the extensive experience gained from KC3. In the coming year the NMIs wishing to participate will be determined and a set of protocols and a transfer standard package developed. Technical Report 23 discusses these activities in more detail.

International Comparisons of Pressure and Vacuum Standards.

In FY00, the Pressure & Vacuum group participated in:

- six CCM Key comparisons spanning the range 10^{-6} Pa to 500 MPa,
- one bilateral comparison with the Czech Metrology Institute,
- two SIM comparisons from atmospheric pressure to 100 MPa, and
- one domestic comparison from atmospheric pressure to 1.4 MPa under NCSL-International.

NIST is piloting three Key comparisons, two of which completed the Draft A phase, and the third nearing completion of the measurement phase. For one SIM comparison, we discovered a transfer package shift necessitating a repeat of the comparison, while the results for the successful NIST-piloted comparison for the NCSL were presented at their annual meeting. For FY01, we will diminish our participation in the CCM Key comparisons as they conclude, while increasing our efforts in SIM and NCSL-International comparisons.

The BIPM/CIPM Working Group for Fluid Flow. In the past year, the newly formed BIPM/CIPM Working Group for Fluid Flow (WGFF), chaired by G. E. Mattingly, has formed its strategy, structure, and schedules to attain its goal of…"providing governments and other parties with secure technical foundations for wider agreements related to international trade, commerce and regulatory affairs". The NMIs participating in the WGFF met for the first time in June 2000 to begin organizing a system of comparisons of national measurement standards for six areas:

flowrate measurements for:

- water
- hydrocarbon liquids,
- low-pressure air, and
- high-pressure natural gas,

and related measurement areas of:

- air speed and
- liquid volume.

Primary and secondary leadership roles in each area were assigned and accepted by respective NMIs. The initial WGFF tasks for the NMIs in each measurement area will be to review the Calibration and Measurement Capabilities (CMCs) of the other NMIs in that area and either accept or express reservations regarding quoted uncertainties. These reservations are then subsequently used to design and conduct Key Comparison (KC) tests that will confirm or refute the suspect uncertainties. Ultimately, when WGFF efforts for the acceptability of the CMCs and the results of the KCs confirm the equivalence of the flow standards in the world's NMIs are made public and available to all, via the internet, measurement-based, non-tariff trade barriers may be eliminated worldwide.

NIST has undertaken a primary role in low-pressure air and a secondary role in high-pressure natural gas. Technical Report 23 reviews these responsibilities in more detail.

Standards for Raman Spectroscopy

CSTL Program: Process Metrology
Authors: *W.S. Hurst; S.J. Choquette (839); E.S. Etz, J. Maslar, V. Podobedov, and D.H. Blackburn (837); and R. McCreery (Ohio State Univ.)*

Abstract: 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 to provide instrument intensity calibration. A chromium-oxide doped glass has been shown to be suitable for use with laser excitation at 785 nm has been developed and shortly will be available as SRM 2241. The fluorescent properties have been tailored to industrial needs, as advised by ASTM E13.08 following a round-robin calibration employing a prototype glass. Critical Raman measurements of organic liquids were completed, from which peak area ratios were extracted. This information is needed by end-users, who will make such measurements as a means of quality control of their calibration process.

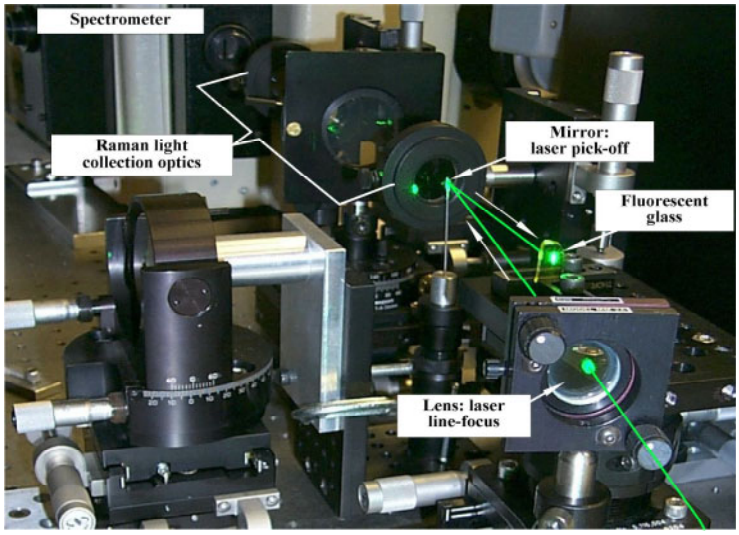


Figure 1. Experimental set up showing use of SRM 2241.

Purpose: Major advances in analytical Raman instrumentation have virtually revolutionized Raman spectroscopic measurement, so that 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. Intensity calibration of Raman spectra can be accomplished using white light sources, but this procedure requires expensive equipment, has a source

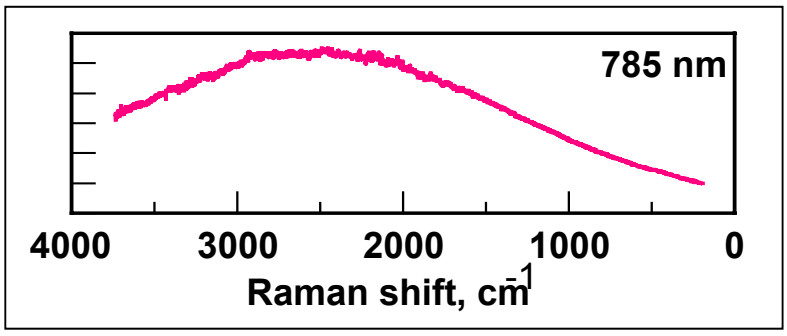
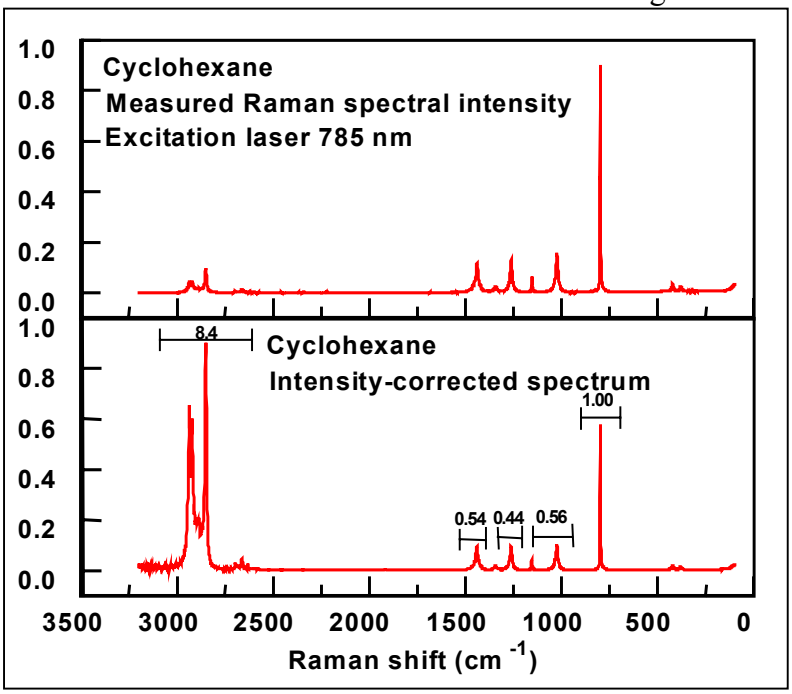


Figure 2. Broadband fluorescence from chromium-oxide glass which light corrected for instrument response.

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 research efforts have focused on the fluorescence spectra of doped glasses that can provide broadband emissions over the common Raman spectral domains. We have shown that these glasses are suitable for certification of a set of Standard Reference Materials (SRMs) traceable to NIST primary radiometric standards. Contact with the Raman community of major chemical industries, instrument manufacturers, regulatory agencies, and initiatives adopted by the ASTM E13.08 Subcommittee on Raman Standards will be maintained so that methods, standards, and techniques developed by NIST are widely accepted by the user community, particularly industrial users.

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 of significantly different design. The details of the fluorescent intensity response and spectral shape of this glass were adjusted to meet the recommendations of the ASTM E13.08 subcommittee, after the results of an ASTM round-robin spectral-intensity calibration test conducted this year were assessed. This glass will be available as SRM 224. It will be provided with a curve expressing its relative irradiance as a function of the Raman shift in wavenumbers (cm^{-1}). Type B systematic errors dominate these measurements and numerous sorts of tests were done to investigate the characteristics of these error sources.



The sensitivity of the spectral response to temperature (15 °C to 40 °C) and to laser excitation wavelength (780 nm to 788 nm) has been measured and also will be provided to users. Measurements of pure organic liquids are expected to provide a test of calibration correctness. The peak area ratios of (mainly) cyclohexane were studied and will provide benchmark data for both values and the appreciable variances of these measurements that are dependent upon the details of individual Raman spectrometer designs and of the experimental apparatus.

Impact: This program will for the first time provide industry with a relatively inexpensive means for calibration of the Raman spectral intensity. This will promote the acceptance of this relatively new (in industry) measurement technique and provide a means for instrument qualification as required by regulatory agencies.

Future Plans: As requested by ASTM E13.08, NIST will next work on intensity standards for excitation wavelengths of 488, 514, and 532 nm (the commonly used argon laser lines) and at

1064 nm. Past work at NIST has indicated the availability of doped-glass systems with usable properties. Further research will be done to find a suitable glass composition for use at 633 nm and 647 nm, commonly used laser source. There is growing interest in Raman imaging systems, particularly for measurements of heterogeneous materials as encountered in biological and semi-conductor work. NIST has had inquiries from manufacturers of these systems, which have an enhanced set of requirements for intensity calibration, and will require further development by NIST.

A New Primary Standard for Gas Flows between 1 g/min and 1600 g/min

CSTL Program: Process Metrology
Author: *J.D. Wright*

Abstract: To enhance our capabilities to realize and disseminate gas flow rate standards a new primary standard is nearing completion. This approach is expected to reduce the measurement uncertainty from 0.20% to 0.05% or better for in the flow range 1 to 1600 g/min (~1 to ~1600 l/min). The system is essentially a "bucket and stopwatch" for gas: steady state flow is diverted by valves for a measured time period into a previously evacuated collection tank of accurately determined volume. Initial and final gas density values are calculated from pressure and temperature measurements in the collection tank are used to calculate the change in the mass of the gas collected. This value and the collection time gives the gas mass flowrate. Although, metrologists have used this method of gas flow measurement for decades, several refinements to the method are anticipated to result in significant reduction measurement uncertainty. Accuracy in temperature measurements of the gas collected is critical. A high stability water bath is an important feature of the system. The relatively small diameter of the collection tanks provides good heat transfer to bring the gas to thermal equilibrium and uniformity despite the inevitable temperature changes caused by the evacuation and filling processes. Bath temperature control capabilities have been demonstrated below the 5 mK level giving a thermal performance that substantially exceeds design targets. In the coming year system performance is expected to also exceed our original design target of 0.05%.

Figure 1. A view of the new gas flow standard. Shown are the temperature controlled water bath, mixers, two sets of gas collection tanks, flow diverter valves, and the data acquisition and control instrumentation (at the far end).

Purpose: Improve NIST gas flow rate standards by a factor of 4 or more to respond to the needs of U.S. flow meter manufacturers and users. Such an improvement in the accuracy of flow meter calibrations supports the U.S. gas flow metering community and assists it in remaining competitive in worldwide gas metrology markets. It is expected that the performance of this system will provide NIST with the ability to disseminate gas flow rate measurement standards at levels that exceed the capability of other NMIs.

Major Accomplishments: Several prototype designs were built and experimentally evaluated, both for the water bath and the gas collection tank. A final system design was completed and the system constructed. Experiments show that the assembled gas collection system provides water temperature stability and uniformity of better than 5 mK, well below the uncertainty goal for this

component (see figure 2). To cover the wide range of flow, the flow standard was designed with two gas collection tanks. The gas collection tanks were designed to have a small enough diameter that thermal equilibrium of the collected gas would be reached in ten minutes or less by heat conduction alone. Evaluation of the real system shows that equilibrium is achieved in about 6 minutes, again better than the design goal.

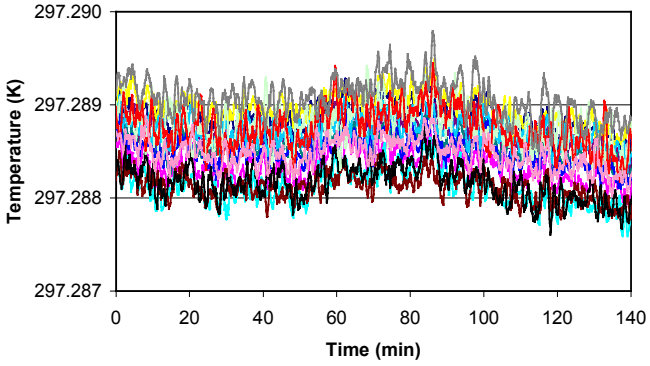


Figure 2. Temperature measurements from 13 thermisters distributed throughout the water bath showing stability and uniformity of about 2 mK.

Impact: The development of the new gas flow standard will allow reduced uncertainties in the NIST calibration service and dissemination of lower uncertainty traceability throughout the domestic flow calibration community. It will serve as a platform for research on improvements in flow meter design. It also places us in an excellent position for our role as the pilot laboratory for low pressure gas flow rate comparisons to be conducted by the Working Group on Fluid Flow of the Consultative Committee on Mass and Related Quantities of the CIPM.

Future Plans: In FY 2002 collection tank volumes will be determined gravimetrically to finalize an initial uncertainty analysis. Subsequent comparison with NIST's current standards will be completed as part of operational testing of the system to characterize performance and verify the uncertainty analysis. The facility will then be available as part of our low gas flow calibration service. All indications are that this will be a low uncertainty, time-efficient and highly automated calibration facility that will meet our customers' needs for many years to come.

Johnson Noise Thermometry

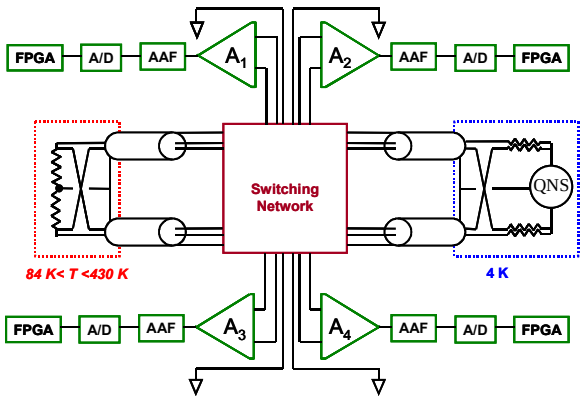
CSTL Program: Process Metrology
Authors: *W.L. Tew, and D.R. White; J. Martinis, S. Benz, and S.W. Nam (814)*

Abstract: The electrical noise (Johnson Noise) power in a resistor is a measure of thermodynamic temperature. The practical implementation of this effect, known as Johnson Noise Thermometry (JNT), has applications both in temperature metrology and in harsh industrial environments. The NIST JNT competence project is a collaboration between CSTL, EEEL, and the MSL of New Zealand, and is focused on the development of a new technique where a synthesized Josephson Voltage Source (JVS) is used to calibrate a noise power correlation instrument. This approach has several technical advantages over conventional JNT techniques and conveys improvements in measurement speed, flexibility, and accuracy. The new approach also uses the calculable properties of the JVS to create a new and different type of noise thermometer in which no fixed points are required, a desirable property for remote and/or harsh-environment applications.

Purpose: Develop a new approach to JNT using Josephson waveform synthesis to address limitations in conventional approaches and to demonstrate its viability for new applications.

Major Accomplishments: This year all the major hardware components were constructed and tested, including JNT probes, a JVS, noise power correlation instrument, and a Ga triple-point system. The various measurement and source sub-systems are ready for integration into a complete instrument system and testing at 302.916 K at NIST-Boulder.

The noise correlation amplifier under construction.



Impact: The short-term impact will be improvements in the domain of noise metrology, as the NIST knowledge base and expertise expanded. The long-term impacts are most likely in those applications where long-term stability at higher temperatures is a critical requirement and where either remote operations or hazardous environmental conditions limit the use and recalibration of conventional material-artifact probes.

Future Plans: The project goals are to achieve a working prototype instrument in Boulder by the end of FY02. The technology will then continue to be perfected as hardware and expertise is transferred to Gaithersburg, and facilities for comparing the JNT-derived temperatures to ITS-90 defined temperatures are developed.

Isotopic Effects in the Realization of the ITS-90

CSTL Program: Process Metrology
Authors: *W.L. Tew, and C.W. Meyer; T. Coplen (USGS); B. Fellmuth (PTB); F. Pavese (IMGC); and A. Szmyrka-Grzebyk (INTiBS)*

Abstract: An ambiguity in the ITS-90 definition of the equilibrium-hydrogen (e-H_2) triple point (13.8033 K) has been identified and quantified. The concentration of deuterium (^2H) in both synthetic and naturally occurring hydrogen is highly variable, with mole fractions of $^2H/^1H$ ranging from 25 µmol/mol to greater than 156 µmol/mol depending on the source. This ambiguity e-H_2)triple point is more than twice as large as the typical expanded (k=2) uncertainties reported by the National Metrology Institutes (NMIs) who realize that fixed point. The nuclear-spin-catalysis requirements to produce para-ortho equilibrium likewise create other ambiguities for the realization of this fixed point. To address these problems, an international collaboration between NIST, PTB (Germany), IMGC (Italy), and INTiBS (Poland) has produced new results on isotopic dependence in the e-H_2 triple point and quantified the size of the catalyst-induced depression. These results impact future changes to the ITS-90 in the cryogenic range and the level of comparability between NMIs realizing ITS-90.

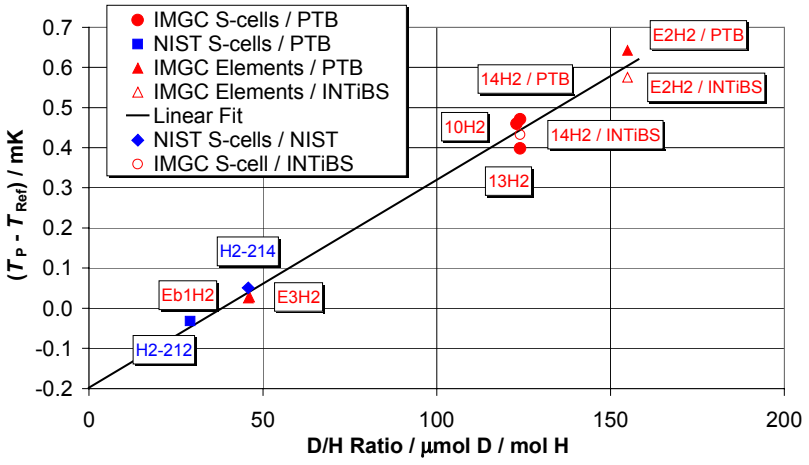


Figure 1. The current results of the international comparison of e-H_2 STPCs as a function of isotope ratio. The legend indicates the origin of the STPC and the NMI which performed the measurement.

Purpose: The definition and measurement ambiguities that have been recently exposed in the e-H_2 fixed points are now recognized as the limiting factors in demonstrating equivalence in calibration capabilities amongst the NMIs in that range of temperatures. The international collaboration underway to overcome these limitations has now established a quantitative basis for interpreting all future e-H_2 fixed point realizations and for making future changes to ITS-90 or developing future temperature scales.

Major Accomplishments: Through a collaboration with the US Geological Survey (USGS), Reston, Virginia, NIST was the first NMI to determine the isotopic composition for the H_2 gas used in the as-disseminated version of the ITS-90. The intercomparison of Sealed Triple Point Cells (STPCs) at PTB demonstrated a high level of agreement between independent realizations by NIST and PTB using a NIST e-H_2 STPC. This international collaboration has now produced the first data set on isotopic and catalytic dependence in the e-H_2 triple point covering the full range of common isotopic compositions.

Impact: This work will result in a proposal for a revision of the definition of the e-H2 fixed points of the ITS-90. Adoption of the proposal would eliminate a significant ambiguity of the ITS-90 and result in superior equivalence of the NIST-disseminated ITS-90 to the realizations of the ITS-90 by other NMIs.

Future Plans: The inclusion of a few more STPCs in the data set for the collaboration, including at least one more each from NIST and NISJ (Japan), will allow a definitive data set to be published establishing a new ITS-90 prescription on the isotopic correction factor for the e-H_2 triple point.

Acoustic Thermometry

CSTL Program: Process Metrology
Authors: *D.C. Ripple, G.F. Strouse, and M.R. Moldover*

Abstract: The International Temperature Scale of 1990 (ITS-90) has uncertainties in the range 300 K to 800 K much larger than either the claimed experimental uncertainties or the reproducibility of Standard Platinum Resistance Thermometers. We seek to reduce the uncertainties in the ITS-90 in the range 300 K to 800 K by a factor of five, through measurement of the thermodynamic temperature of a monatomic gas to high accuracy using acoustic resonance techniques. In FY01, testing of the Acoustic Thermometer up to 575 K was completed with excellent results, including measurement of impurities of gas directly flowing from the high-temperature resonator, solution of problems with unsatisfactory signal levels from acoustic and microwave transducers, completion of acoustic test measurements over a wide range of acoustic frequencies and gas pressures, and completion of microwave measurements of thermal expansion of the acoustic resonator. Upon completion, this work will provide the basis for an improved International Temperature Scale with superior thermodynamic self-consistency.

Figure 1. The 3 liter acoustic resonator, resting inside the lower part of a pressure vessel.

Purpose: We seek to reduce large uncertainties in the ITS-90 in the range 300 K to 800 K by a factor of five, through measurement of the thermodynamic temperature of a monatomic gas to high accuracy using acoustic and microwave resonance techniques.

Major Accomplishments: We have completed testing of the Acoustic Thermometer up to 575 K with highly satisfactory results. In this final phase of testing, we successfully:

- measured impurities of gas directly flowing from the high-temperature resonator and verified that these impurities may be reduced to acceptable levels by maintaining a gas flow,
- solved problems with unsatisfactory signal levels from acoustic and microwave transducers,
- completed acoustic test measurements over a wide range of acoustic frequencies and gas pressures, and
- completed microwave measurements of thermal expansion of the acoustic resonator, demonstrating that the resonator is dimensionally stable.

Impact: This experiment will serve as the basis for a revision of the International Temperature Scale of 1990 with much improved thermodynamic consistency in the range 300 K to 800 K. The results of this experiment will be incorporated into the next temperature scale both in adjustments to the assigned temperature values of fixed points and in an improved reference function for standard platinum resistance thermometers, which are widely used as reference standards in industrial laboratories.

Future Plans: We are presently completing the furnace that encloses the acoustic resonator. Following a brief period of testing, we will redetermine the thermodynamic temperatures of the gallium, indium, and tin fixed points in time for presentation at the 8th International Temperature Symposium in October of 2002.

Maintenance and Dissemination of the International Temperature Scale of 1990 (ITS-90)

CSTL Program: Process Metrology
Authors: *D C. Ripple, W.C. Ausherman, S.L. Cooper, K.M. Garrity, J. Lippiatt, C.W. Meyer, G.F. Strouse, W.L. Tew, and C.D. Vaughn*

Abstract: A primary role of the NIST Thermometry Group is to maintain the ITS-90 and to disseminate the scale to a broad variety of customers. We also are actively engaged in research and educational activities that enable industry to achieve traceability to NIST temperature standards. Significant accomplishments in these support activities included research on rugged fixed-point cells for the U.S. Army Combined Calibration Group, analysis and publication of results on the non-uniqueness of the ITS-90 in the range 660 °C to 962 °C, a doubling of downloadable NIST temperature-related publications on the NIST Thermometry Group website, and presentation of ten papers at the TEMPMEKO 2001 Conference in Berlin on topics ranging from fundamental aspects of the ITS-90, to industrial thermometer calibrations, and to humidity measurements.

Purpose: Temperature is one of the base units of the SI metric system. A primary role of the NIST Thermometry Group is to maintain the ITS-90, and to disseminate the scale to a broad variety of customers through calibration services and Standard Reference Materials. We also are actively engaged in research and educational activities that enable industry to achieve traceability to NIST temperature standards.

Major Accomplishments: Calibration services continued through FY01. Significant additional accomplishments included the following.

As part of a research project for the Combined Calibration Group (CCG) of the U.S. Armed Forces, three small and rugged fixed-point cells (water, gallium, and indium) were investigated for use in dry well block calibrators to provide single-point calibrations for industrial platinum resistance thermometers (IPRTs) for the CCG mobile calibration facilities. The expanded uncertainties (k=2) of the cells do not exceed 0.01 °C.

Preliminary results of investigation of the non-uniqueness of the ITS-90 using high temperature SPRTs (HTSPRTs) in the range 660 °C to 962 °C were reported at the TEMPMEKO 2001 conference. The results of the investigation show that the non-uniqueness values of the scale are similar to the measurement uncertainties, and are not more than 2 mK to 3 mK.

The website for the NIST Thermometry Group was substantially enhanced during FY01, including doubling of downloadable NIST temperature-related publications in response to our customer's requests for greater electronic access to NIST publications.

At the TEMPMEKO 2001 Conference in Berlin, ten papers were presented. The subject matter published by the NIST Thermometry Group ranged from fundamental aspects of the ITS-90, to industrial thermometer calibrations, and to humidity measurements.

Impact: The work of the NIST Thermometry Group on the ITS-90 is critical for providing the top level of traceability of temperature for industry. Our education and research activities in support of the ITS-90 and related topics serve as resources for continued improvements by industry in their own realizations or disseminations of the ITS-90.

Future Plans: A major task in FY02 will be reviews of the NIST Thermometry Group Quality Systems both within NIST and by an international panel, as part of the NIST self-declaration of quality. We will also be preparing at least four manuscripts, for submission to the 8th International Temperature Symposium, describing our ITS-90 dissemination mechanisms or the properties of secondary thermometers.

Initiating a freeze of a tin freezing point cell, as part of the calibration of an SPRT on the ITS-90.

Fabrication of a center heater core for a new type of high-temperature furnace, used in the realization of the ITS-90.

Fixed-Point Cell Mini-Workshop

In August 2001, the first ITS-90 Fixed-Point Cell Mini-Workshop was given in the NIST Platinum Resistance Thermometry Laboratory. This workshop was designed to give four participants intensive "hands-on" laboratory training in the realization and uncertainties of ITS-90 fixed-point cells (234.3156 K to 692.677 K). The four participants were from a two secondary laboratories (Troemner Laboratories, Hart Scientific) and a pharmaceutical company (Abbott Laboratories) in the US that provide ITS-90 based calibrations of SPRTs for their customers.

Standards for concentration of water vapor in gases

CSTL Program: Process Metrology
Authors: *J.T. Hodges, G.E. Scace, W.W. Miller, and J. Valencia-Rodriguez (Guest Researcher)*

Abstract: The most fundamental physical quantity in humidity metrology is the mixing ratio of a gas mixture, which is defined as the mass of water vapor per mass of dry gas. Through measurements of mass, pressure, temperature and length, this derived quantity can be expressed in terms of fundamental SI units. The NIST Thermometry Group is actively upgrading its instrumentation to generate and detect water vapor at known mixing ratios. In the past year, we have completed the uncertainty analysis of the new Low Frost-Point Generator (LFPG) and have completed all of the subsystems of the NIST Gravimetric Hygrometer. The LFPG provides a precise and reproducible source of water vapor mole fraction in the range 5 nmol/mol to 4 mmol/mol for research, calibration of transfer standards, and testing and development of new humidity instrumentation. The Gravimetric Hygrometer will be a primary standard at NIST in the range 10 micromol/mol to 10 mmol/mol that will enable linking of the dew or frost-point temperature set by the LFPG and other NIST humidity generators to the mixing ratio.

Purpose: Previous NIST standards for water vapor are over 40 years old and did not extend to low water vapor levels that are critical in such areas as semiconductor processing. Implementation of the NIST Low Frost-Point Generator in regular calibration and research use is critical to providing industry NIST traceability for measurements of low levels of water vapor. Development of the NIST Gravimetric Hygrometer will provide improved uncertainties and quality assurance to a wide range of humidity calibration customers.

Major Accomplishments: A new system was constructed to replace and upgrade a gravimetric-based primary standard formerly used at NBS/NIST. This new, fully automated gravimetric apparatus enables the measurement of mixing ratio produced by NIST standard generators and consists of a gas drying train followed by a piston-cylinder arrangement. The mass of water vapor collected in the drying train is determined by weighing collection tubes, and the mass of dry gas exiting the collection tubes is calculated from measurements of the pressure, temperature and volume of the sample stream. Based on tests performed in FY01, the dry gas collection system has an expanded (k=2) relative uncertainty of better than 0.1 %, and can be used as a flow standard in the range 0.1 to 2 L min^{-1}. A custom-designed weighing apparatus was built and fully tested, to facilitate automated weighing of the water vapor collection tubes.

Figure 1. Close-up view of Hg-sealed pistons and prover tube assembly used for dry-gas mass determination in the NIST Gravimetric Hygrometer.

In FY 2001, a detailed uncertainty analysis of NIST's low frost-point humidity generator (LFPG) was completed. This thermodynamically based standard generator provides a precise source of water vapor mole fraction in the range 5 nmol/mol to 4 mmol/mol for research, calibration of transfer standards and testing and development of new humidity instrumentation. Mixtures of specified humidity are generated by saturating air or nitrogen with water vapor over a planar ice surface that is maintained under conditions of constant temperature and pressure.

Impact: The anticipated operation of the gravimetric hygrometer will provide NIST with a primary humidity standard with improved uncertainty. This instrument will be used to better characterize NIST humidity generators, giving humidity calibration customers improved uncertainties and greater quality assurance. The completion of the uncertainty budget of the LFPG now enables use of this generator as a reliable and well-characterized tool in the calibration of customer devices, providing traceability to NIST calibration customers at lower water vapor levels than previously available. The LFPG has already been used as the reference standard for a comparison done in collaboration with SEMI of dilution-based humidity sources widely used in the semiconductor industry and in-situ reference standards operating in the 10 to 100 ng/g region.

Future Plans: Routine operation of the gravimetric hygrometer system is anticipated in FY 2002. Initial application of the system will be used to measure the output of standard humidity generators such as the LFPG. This will provide an independent check upon the LFPG uncertainty analysis discussed above, and will provide the basis for absolute determination of optical absorption line strengths in terms of water vapor concentration and CRDS measurements of sample absorbance. The LFPG will be in regular use in FY02 studying the characteristics of a variety of commercial hygrometers designed for detection of trace water vapor.

Cavity Ring-Down Spectroscopy (CRDS) as a primary method for the determination of water vapor concentration

CSTL Program: Process Metrology (Microelectronics)
Authors: *J.T. Hodges, W.W. Miller, A.C.R. Pipino, G.E. Scace, and H. Layer (Guest Researcher)*

Abstract: Water vapor has an absorption spectrum comprising thousands of distinct rovibronic absorption transitions in the visible and near-infrared spectral regions. By combining high spectral resolution with high precision absorbance measurements, water vapor concentration can be determined independently of the composition of the carrier gas. To this end, we are developing frequency-stabilized single-mode cavity ring-down spectroscopy (SM-CRDS) for the measurement of water vapor concentration in various media. SM-CRDS is a cavity-enhanced optical absorption technique that has high sensitivity and frequency resolution, fast response, specificity, and probes a compact well-defined volume. Unlike other absorption spectroscopies, the measured absorbance does not depend upon the source laser intensity, the quantum efficiency or absolute responsivity of the detection system, or geometrical factors. We have successfully fabricated and tested a length-stabilized SM-CRDS system, based on a cw diode laser and optimized for detection of water vapor.

Purpose: Our work has two objectives. First, we are developing a primary method for optically determining the absolute water vapor concentration in the range 1 nmol/mol to 10 mmol/mol. In this range, we expect CRDS to be the primary standard of humidity at NIST. Second, we expect the metrological techniques that we are developing to have broad applications in a variety of spectroscopic applications to trace gas analysis where sensitivity and accuracy are both important.

Major Accomplishments: In FY 2001, a cw diode-laser based SM-CRDS system was assembled. This system consists of a commercial external cavity diode laser and a doubly resonant ring-down cavity that is actively length-stabilized with respect to a frequency stabilized HeNe laser. The sample cell is constructed of all-metal, vacuum-compatible components and is designed for handling trace quantities of H_2O. Length stabilization of the ring-down cavity is realized using closed-loop control of a piezoelectric-actuated mirror assembly. In this way, the longitudinal mode spacing of the stabilized ring-down cavity provides a well-defined and stable frequency interval which can be used to specify the wavelength dependence of the absorption spectra with high precision. Importantly, unlike other commonly employed CRDS techniques, the SM-CRDS method developed here exploits the high frequency resolution of ring-down cavities (1 to 10 kHz) by actively locking the ring-down cavity length to a frequency-stabilized laser. This ultimately enables an extremely precise determination of the frequency, or wavelength, of the absorption lines studied. Finally, because the cw probe laser has a narrow bandwidth compared to the ring-down cavity mode spacing, single-mode excitation of the ring-down cavity is enabled, a condition that NIST has previously shown to optimize measurement precision.

Impact: The system constructed in FY01 is an important milestone in the application of CRDS to practical metrology applications at the highest levels of accuracy. This work will lead to primary standards for humidity down to 1 nmol/mol. Standards at this low level are needed to pro-

vide reliable traceability for sensing of trace water vapor in semiconductor processes gases and for specialty gas production. However, there is presently no other feasible primary standard for humidity measurement at the 1 nmol/mol level. For semiconductor processes involving reactive or corrosive gases, the CRDS methods developed will also be useful in characterizing water vapor or other impurities in gases are not suited for probing with other forms of spectroscopy.

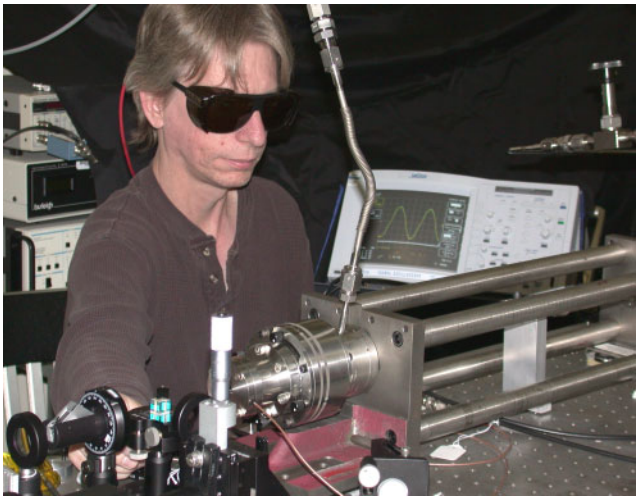


Figure 1. The NIST actively length stabilized SM-CRDS apparatus.

Future Plans: In FY02, our primary goal is to obtain quantitative measurements of the spectral absorption lines of water. To achieve the high performance promised by CRDS, we will complete our ongoing development of a cw diode laser frequency locked to the ring-down cavity.

Results of the NIST-SEMI comparison of dilution-based sources for trace humidity

CSTL Program: Microelectronics
Authors: *J.T. Hodges, P.H. Huang, W.W. Miller, and G.E. Scace*

Abstract: Industrial laboratories engaged in calibration or research involving detection of trace levels of water vapor rely on dilution-based humidity sources. The NIST-SEMI comparison studied the performance of dilution-based sources against NIST's thermodynamically based source. As part of this work, a new experimental technique that references the output of dilution-based humidity generators to the output of NIST's low frost-point generator (LFPG) was developed. The method is capable of resolving fractional differences of approximately 1 %, for humidity generators covering the mole fraction range 10 nmol/mol to 100 nmol/mol, and uncertainties in flow metering and background water vapor present in the carrier gas were identified as limiting effects. The results of the NIST-SEMI comparison demonstrates to the semiconductor processing industry, and other users of low moisture concentration process gases, the reliability of dilution-based humidity generation techniques. In FY02, the methods developed will result in a calibration service to industry that will provide traceability to NIST standards.

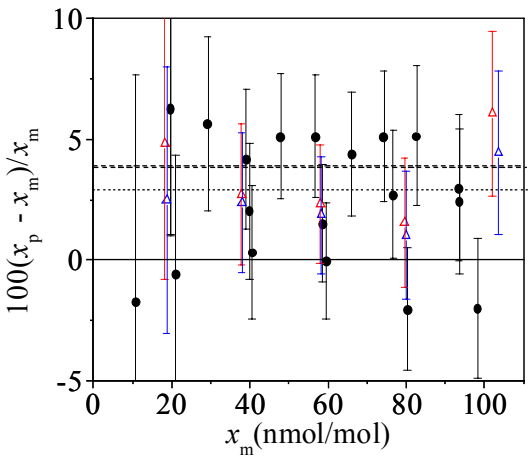


Figure 1. Results from comparison of two permeation tube generators with the NIST-LFPG. The horizontal axis is the mole fraction of water vapor in N_2, and the vertical axis is the % deviation with respect to the expected mole fraction.

Purpose: Industrial laboratories engaged in calibration or research involving detection of trace levels of water vapor rely on dilution-based humidity sources. These sources have not previously been compared to NIST standards. The purpose of the NIST-SEMI comparison is to critically and quantitatively study the performance of dilution-based sources relative to NIST's thermodynamically based source.

Major Accomplishments: A new experimental technique that references the output of dilution-based humidity generators to the output of NIST's low frost-point generator (LFPG) was developed in FY01. Such trace humidity generation devices are widely used by high-purity gas manufacturers and by semiconductor-related industries in the calibration of high-sensitivity hygrometers. The method developed here is capable of resolving fractional differences of approximately 1%, for humidity generators covering the mole fraction range 10 to 100 nmol/mol, and uncertainties in flow metering and background water vapor present in the carrier gas were identified as limiting effects.

Impact: The results of the NIST-SEMI comparison provide the semiconductor processing and high purity gas manufacturing industries with evidence of the reliability of dilution-based humid-

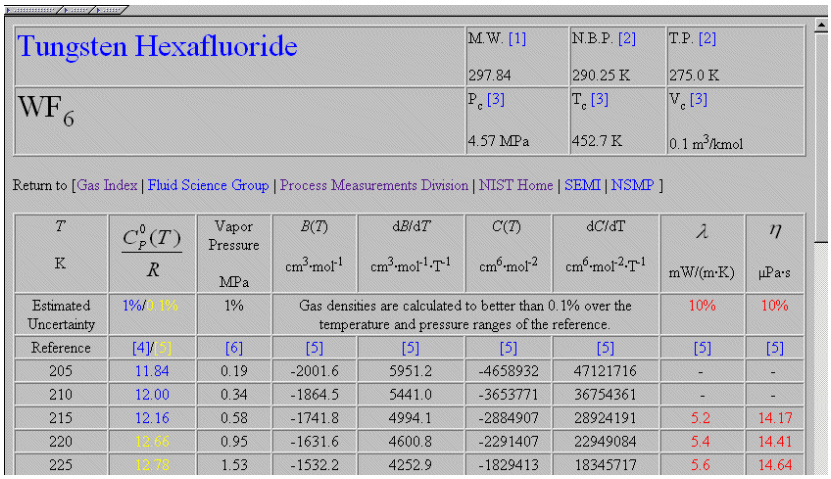
ity generation techniques. The methods developed will result in a calibration service to industry that will provide traceability to NIST standards.

Future Plans: In FY02, the full results of the NIST-SEMI comparison will be published. The method developed for this comparison will provide the basis for a new, low cost humidity calibration service that will enable direct traceability of portable humidity standards to NIST trace humidity standards.

Thermophysical Properties of Gases used in Semiconductor Processing

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

Abstract: CSTL is measuring the thermophysical properties of the gases used in semiconductor processing. The resulting data will rationalize the calibration of mass flow controllers (MFCs) and improve the modeling of chemical vapor deposition (CVD). As data are acquired, they are posted on the web site http://properties.nist.gov/semiprop. (Fig. 1.) Interactions with industry groups provide NIST with recommendations for the gases and the properties to be studied as well as targets for the accuracy of the data. The gases include process gases, "surrogate" gases used for calibration, and binary mixtures of process and carrier gases. The required properties include: speed-of-sound, heat capacity, density (equation of state), viscosity, and thermal conductivity.



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 $cm^6 \cdot mol^{-2} \cdot T^{-1}$	λ mW/(m·K)	η µPa·s
Estimated Uncertainty	1%/0.1%	1%	Gas densities are calculated to better than 0.1% over the temperature and pressure ranges of the reference.				10%	10%
Reference	[4]/[5]	[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	12.33	0.95	-1631.6	4600.8	-2291407	22949084	5.4	14.41
225	12.50	1.53	-1532.2	4252.9	-1829413	18345717	5.6	14.64

Figure 1. Sample Web Page from database located at the URL http://properties.nist.gov/semiprop/

Purpose: The *National Technology Roadmap for Semiconductors* identifies "Equipment Modeling" as first in a list of "Technology Requirements" and states that "the drivers for equipment modeling are *equipment design*, *process control*, . . . " The *Roadmap* indicates that continuing research is needed to obtain experimental data for "transport and thermal thermodynamic and transport property data for the gases used in semiconductor processing.

During May 2000, Dr. Robert Berg of CSTL organized a workshop entitled "Mass Flow Measurement and Control for the Semiconductor Industry." At the workshop, representatives of industry identified the properties and their allowable uncertainties for accurately modeling MFCs and related equipment. The workshop's list of properties is:

- heat capacity at constant pressure $C_p(T)$ (±0.1%),
- equation of state $\rho(T,p)$ for predicting gas densities (±0.1 %),
- viscosity $\eta(T)$ (±0.5%), and
- thermal conductivity $\kappa(T)$ (±0.5%).

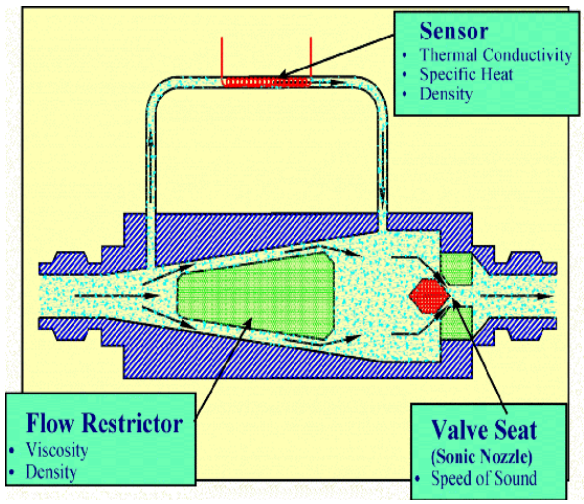


Figure 2. Components of a generic mass flow controller (MFC) and the thermophysical properties required to model them.

Figure 2 indicates that these are the thermophysical properties necessary to model the performance of the components of a generic MFC. A central recommendation in the MFC workshop report was that values of these properties be made available from a 'standard' source, i.e., accessible to all sectors of the semiconductor processing industry.

Major Accomplishments: Speed of sound measurements have been completed in the three surrogate gases and the seven process gases listed in Table 1. Figure 3 shows a fraction of the results for NF_6. 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 with an uncertainty of 0.1 %.

Computer programs have been developed to correlate the speed-of-sound data with model, hard-core Lennard-Jones intermolecular potentials for calculation of second and third virial coefficients and transport properties from the model intermolecular potentials.

Table 1. Ranges of speed-of-sound data.

Gas	Temperature Range (K)	Maximum Pressure, MPa
CF_4	300 - 475	1,500
C_2F_6	210 - 475	1,500
SF_6	230 - 460	1,500
Cl_2	260 - 440	1,500
HBr	230 - 475	1,500
BCl_3	300 - 460	1,500
WF_6	290 - 420	300
C_2H_4O	285 - 440	1,000
NF_3	200 - 425	1,600
$Ga(CH_3)_3$	340 - 420	900

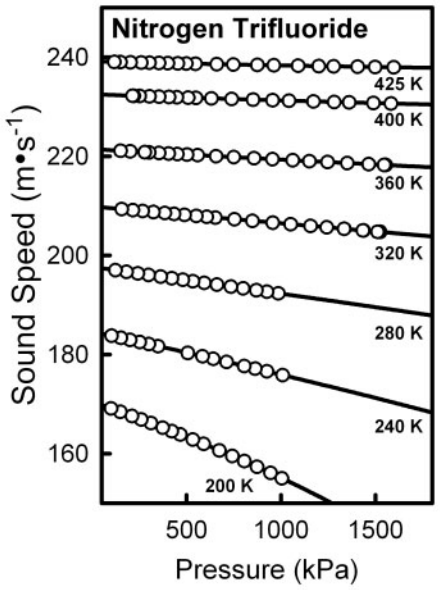


Figure 3. Speed of sound in NF_3 as a function of pressure along isotherms.

To determine gas transport properties, an acoustic viscometer based on Greenspan's design was completed. To optimize the viscometer's performance, we tested several geometries and acoustic models. Figure 4 shows that all of the data from the final acoustic viscometer for several test gases are within ±0.5 % of reference data from the literature.

A second generation Greenspan viscometer is now being constructed out of Monel which will allow us to measure the viscosities of the corrosive process gases.

The results of this research have been disseminated by six publications in professional journals and three talks at professional meetings. An on-line database of the results is available on the internet at http://properties.nist.gov/semiprop/

John Hurly, a member of our group, 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.

Future Plans: During FY02, we shall use the Greenspan viscometer to measure the viscosity of the highest-priority surrogate gases and process gases. For those process gases for which no viscosity data exist, the uncertainty of the viscosity will be reduced from an estimated 10 % to approximately 0.5 %.

During FY02, we shall develop an acoustic resonator optimized to measure the thermal conductivity of surrogate gases and process gases.

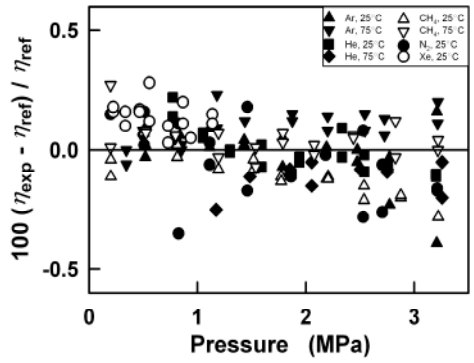


Figure 4. Percentage deviation of viscosities measured with the Greenspan viscometer from reference values of the viscosity.

Models and Data for Semiconductor Processing

CSTL Program: Microelectronics
Authors: *R.W. Davis, J.E. Maslar, and E.F. Moore; D.R. Burgess, Jr. (838); D. Kremer, and S.H. Ehrman (University of Maryland)*

Abstract: The Semiconductor Industry Association's 2000 International Technology Roadmap for Semiconductors identifies the need for a more fundamental understanding of reactor contaminant formation and transport. Process models and computer codes now offer efficient and effective tools with which to improve the understanding of semiconductor processes and process tools. The purpose of this numerical/experimental project is to expand the basic understanding of, and develop a predictive capability for, gas-phase generated microcontaminants in rotating disk thermal chemical vapor deposition (CVD) reactors. Recent accomplishments include excellent comparisons between experimental temperature profiles obtained via Raman spectroscopy and computed profiles utilizing a new multi-dimensional reacting flow code developed at NIST. This code forms the basis for a unique multidimensional microcontamination model that has recently undergone its first successful operational test. This model, unlike the already existing one-dimensional micro-contamination model, is capable of predicting contaminant dynamics throughout the rotating disk reactor, not just in its central region. These accomplishments should ultimately result in an improved ability to adjust semiconductor-processing environments so as to reduce defects and thus improve yields.

Purpose: The purpose of this numerical/experimental project is to acquire an improved understanding of, and develop a predictive capability for, gas-phase generated microcontaminants in rotating-disk thermal chemical vapor deposition (CVD) reactors. Microcontaminants in thermal CVD reactors are being investigated both numerically and experimentally in order to reduce defects during semiconductor processing.

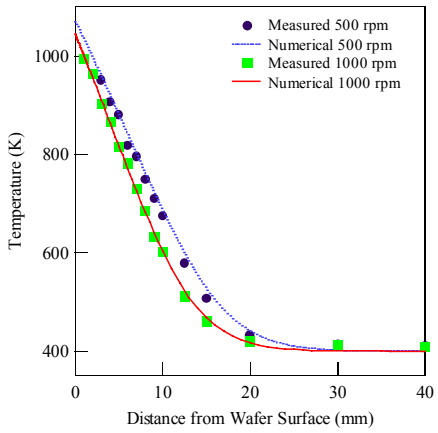


Figure 1. Comparison of model prediction with experimental results.

Major Accomplishments: Experimental Raman spectroscopy temperature measurements in the rotating disk reactor have compared very well with computed temperature profiles obtained from a new multidimensional reacting flow code developed at NIST (see figure). This flow code forms the basis for a unique new multi-dimensional micro-contamination model for this type of reactor. Unlike the previous one-dimensional micro-contamination model utilized for this investigation, this new model can simulate particle behavior throughout the reactor, not just in the central region. The multidimensional model has undergone its first successful operational test, with particle number concentrations and size distributions being predicted inside the entire reactor geometry. These compared well with results from the 1-D model along the centerline.

Impact: These accomplishments will result in an enhanced understanding of microcontaminant behavior in thermal CVD reactors, and thus lead to improvements in semiconductor process control for defect reduction.

Future Plans: This activity will be redirect to focus on advanced interconnect deposition chemistry, where NIST expertise can make a substantial industry impact.

Development of Quantitative Measurements for Semiconductor Fabrication Process Control

CSTL Program: Microelectronics
Authors: *R.F. Berg, D.S. Green (University of Maryland), and J.P. Looney*

Abstract: The semiconductor industry desires real-time quantitative monitoring and control of process gases, however, such diagnostic tools do not yet exist. CSTL is developing the requisite measurement capabilities to control semiconductor fabrication processes and demonstrate them in an actual WF_6 CVD process tool in collaboration with the University of Maryland. In FY01, it was demonstrated that residual gas analyzers could be used to monitor process gases and provide real-time data to control film thickness within 1-2% of set point, which is very close to achieving the industrial target on accuracy. In response to the mass flow controller (MFC) community, we have made significant strides in improving our primary flow standards, improving our transfer standards, and restoring our capability to perform on-site customer proficiency tests. We have commissioned a new gravimetric primary flow standard, confirming its performance against the prevailing constant pressure primary standard. A new transfer standard has been developed and used it to reveal a significant systematic error in the flow standards of a large manufacturer of mass flow controllers during an on-site test. This device has also been used to perform a bilateral comparison with Italian national standards.

Purpose: We wish to develop measurement capabilities that enable real-time, *in-situ* schemes to control semiconductor fabrication processes, by building upon competence in optical diagnostics and flow measurement techniques. The increasing complexity of vacuum processing, most notably in the semiconductor industry, requires real-time monitoring and control of process gases. We previously demonstrated that residual gas analyzers (RGAs) could be made quantitative for *in-situ* monitoring of reaction products, but the 5-10% measurement imprecision was unacceptably large for process control. Optical techniques are promising, but realizing their potential requires a better understanding of the factors limiting their performance. For gas flow, MFC manufacturers have stated the need for improved national standards for gas flow. This includes primary standards at NIST and secondary standards that transfer NIST accuracy to industry.

Major Accomplishments: The cavity-ring-down approach under development at NIST involves developing frequency and cavity locking methods for continuous wave diode lasers to enable measurement of ring-down signals. This has been quite challenging, but temperature and frequency locking electronics were fabricated during this reporting period. In a parallel approach, newly available (and heretofore non-existent) diode lasers with integral frequency-locking capabilities were acquired. The majority of a system for handling and metering wet HF was also constructed; HF is the principle species of interest in the Chemical Vapor Deposition (CVD) tool at the Univ. of Maryland (UMD).

At UMD, improvements to the CVD tool were completed in preparation for the optical diagnostic system. Yield rates were increased, bringing them in line with industrial processes. Relevant gas concentrations were increased, boosting measurement sensitivity and reducing measurement error. Thus, film thickness, controllable to 10% last year, can now be controlled to 2%. In addi-

tion, an acoustic composition measurement technique was successfully tested, which will allow complementary measurements for the optical system being developed at NIST.

A new gravimetric primary standard for low gas flow rates was built and tested. The methods to measure and control pressure in the existing constant-pressure standard also were improved, which now allow for measurements with helium. Nitrogen flow comparisons between these two independent primary standards show agreement to approximately 0.05%.

A new transfer standard employing quartz capillary flow impedances (see figure) was fabricated and characterized. The new geometry allows a model more accurate than that used for the previous transfer standard. Tests also showed that temperature-induced errors of the transfer standard are less than 0.01% per Kelvin, which is negligible. Measurements with helium are underway, and argon and sulfur hexafluoride tests are planned. The new transfer standard was used in a successful comparison with the flow standards of a large manufacturer of MFCs.

Impact: Our measurements have demonstrated that real-time process control of wafer thickness is possible with existing RGA instrumentation. This is a significant accomplishment. In addition, our new flow standards have been developed in direct response to recent industrial input (R.F. Berg, D.S. Green, and G.E. Mattingly, "Workshop on mass flow measurement and control for the semiconductor industry", *NIST Special Publication 400-101,* 2001) and have already affected the primary standards of one OEM manufacturer of MFCs.

Future Plans: Further refinements shall be made with the RGA-based CVD system at the University of Maryland, and composition measurements will be compared with acoustic-based measurements. Regarding flow standards, we shall begin the design and construction of a more robust transfer-standard package with an eye toward using this for more extensive on-site proficiency tests.

New quartz capillary flow impedance

Publications:

R.F. Berg and S.A. Tison, "Laminar flow of four gases through a helical rectangular duct", *AIChE Journal* **47**, 263 (2001).

R.F. Berg, D.S. Green, and G.E. Mattingly, "Mass flow research and standards:
NIST workshop results", *Future Fab International*, edition 10 (2001).

R.F. Berg, D.S. Green, and G.E. Mattingly, "Workshop on mass flow measurement and control for the semiconductor industry", *NIST Special Publication 400-101* (2001).

J.T. Herron and D.S. Green, "Chemical Kinetics Database and Predictive Schemes for Humid Air Plasma Chemistry. Part II. Neutral Reactions," *Plasma Chemistry & Plasma Processing* **21**, 459 (2001).

Surface Temperature Measurements using RTP

CSTL Program: Microelectronics
Authors: *K.G. Kreider, and C.W. Meyer; D.P. DeWitt, and B.K. Tsai (844)*

Abstract: This work is intended to improve the accuracy of wafer surface temperature measurements, with emphasis in the area of rapid thermal processing (RTP) of semiconductors. We have developed and patented a new artifact - a thin-film thermocouple calibration wafer for use in the calibration of lightpipe radiation thermometers (LPRT) in RTP tools. During the last year we investigated the effect of different silicon wafer emissivities and the effect of low emissivity films on RTP wafer temperature measurements. These tests were performed in the NIST RTP test bed. We used a NIST thin-film thermocouple calibration wafer to calibrate the lightpipes *in situ.* We found differences of up to 36 °C at 900 °C in the LPRT measurements due to the low emissivity films. A model of the wafer temperature measurement was developed to provide insight into the effects of wafer emissivity on LPRT measurements in RTP tools. We also worked this year with Vortek Industries, SEMATECH, and University of Texas to evaluate our thin-film calibration wafer under industrial conditions. In both projects we designed and supplied the calibration wafer and assisted the user in its application.

Purpose: The goal of the CSTL work is to improve the accuracy of wafer surface temperature measurements, with emphasis in the area of rapid thermal processing (RTP) of semiconductors. The semiconductor manufacturing industry requires improved process measurement accuracy of silicon wafer temperatures due to increasingly stringent dopant diffusion requirements critical to product quality and device performance. As a result, the industry has an uncertainty requirement of 2 °C at 1000 °C for RTP for the future generation of semiconductor devices.

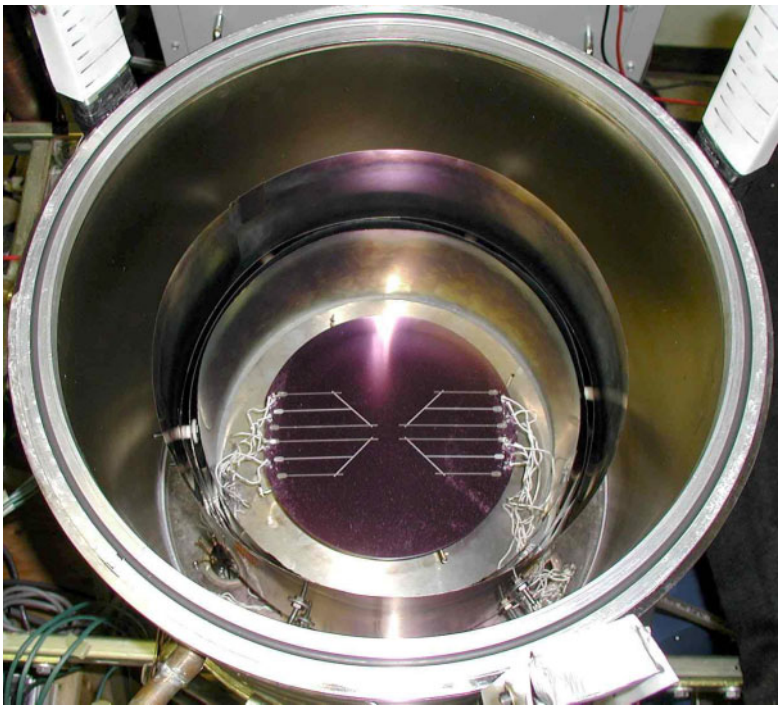


Figure 1. The NIST thin-film thermocouple calibration wafer in the SEMATECH rapid thermal processing (RTP) testbed is being used for evaluation of commercial lightpipe radiation thermometers at the University of Texas.

Major Accomplishments: Watlow Gordon has licensed the NIST patent on the thin-film calibration wafer for RTP temperature measurements.

We have given guidance to the semiconductor manufacturing industry on the effects of emissivity on temperature measurements in rapid thermal processing tools.

Our temperature measurement calibration technology has

been demonstrated in the ISMT (SEMATECH) test bed and the arc-heated Vortek Industries RTP pulse annealer.

The semiconductor industry has recognized the advantage of accurate temperature measurements and traceability to ITS-90 to facilitate improvements in both tool-to-tool and production line-to-production line consistency of operation.

Impact: A SEMATECH program manager has stated that the NTRS Roadmap goal for temperature measurement accuracy is within reach because of our work.

Future Plans: We plan to continue our work with industrial partners in order to develop measurement techniques for temperature calibration in their tools. We are assessing each of the components of the uncertainty of our *in situ* calibration technology and developing methods to reduce that uncertainty.

Plasma Process Metrology

CSTL Program: Microelectronics
Authors: *M. Sobolewski, and K. Steffens; J. Olthoff, Y. Wang, L. Christophorou, and A.Goyette (811); and E. Benck (844)*

Abstract: Advanced measurement methods, data, and models are needed by the semiconductor industry to characterize plasma etching and deposition processes, enabling continued progress in model-based plasma reactor design and plasma process optimization and control. CSTL's Process Measurements Division, in collaboration with EEEL and PL, provide the measurement methods, data, and models needed by our industrial customers.

This year we performed a rigorous test of the ability of models to predict ion kinetic energies in high-density plasmas. Energetic ions play a crucial role in plasma etching and other plasma processes. Our tests showed that ion energy distributions predicted by simple, commonly used models did not agree with measurements. A more sophisticated model, however, did accurately predict ion energy distributions. The model, developed at NIST, can be adapted for use in commercial plasma simulations, and also serves as the basis for new methods for *in situ* monitoring of ion energies.

Also we have extended our capabilities for monitoring spatially resolved radical densities in plasmas using 2-D planar laser-induced fluorescence (PLIF). Using a tunable wavelength laser, we are now able to obtain PLIF images of CF, in addition to CF_2. Both CF and CF_2 are important precursors for the formation of the fluorocarbon polymer layer which provides selectivity during oxide etching and is the basis for plasma deposition of low-k fluorocarbon films. The comparison between CF and CF_2 gives insight into the different roles played by the two radicals, providing guidance for selection of precursor and processing conditions.

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: This year we performed a rigorous test of the ability of models to predict ion kinetic energies in high-density plasmas. Energetic ions play a crucial role in plasma etching and other plasma processes. Ions exiting the plasma are accelerated to high energies by strong, radio-frequency electric fields in plasma sheaths, thin regions located at the boundaries of

plasmas. The complicated ion dynamics in the sheath regions are usually modeled using simplifying assumptions that have never been sufficiently validated. Our tests, performed in CF_4 discharges, showed that ion energy distributions predicted by simple, commonly used, analytical sheath models did not agree with measurements. A more sophisticated model, however, did accurately predict the behavior of measured ion energy distributions and their dependence on frequency, sheath voltage, ion current density, and ion mass. The model, developed at NIST in previous years, can be adapted for use in commercial plasma simulations, and also serves as the basis for new methods for *in situ* monitoring of ion energies at wafers during plasma processing.

Also this year we have extended our capabilities for monitoring spatially resolved radical densities in fluorocarbon plasmas using 2-D planar laser-induced fluorescence (PLIF) imaging. With the implementation of a tunable wavelength laser, we are now able to obtain PLIF images of the CF radical, in addition to CF_2. Both CF and CF_2 are important precursors for the formation of the fluorocarbon polymer layer which provides selectivity during oxide etching and is the basis for plasma deposition of low-dielectric-constant fluorocarbon films. Currently, measurements of spatially resolved CF density have been made in CF_4, CF_4/O_2 and C_4F_8 plasmas, investigating the effects of pressure and power, and the presence of oxygen feedgas and silicon wafers. The comparison between CF and our additional results on CF_2 gives insight into the different roles played by the two radicals, providing guidance for selection of precursor and processing conditions. PLIF images of the two radicals also provide a useful data set for quantitative validation of 2-D plasma simulations.

Other accomplishments this year included the development of new sub-millimeter wave spectroscopic techniques for etching plasmas and assessments of fundamental data on electron interactions with CF_3I and c-C_4F_8.

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 were used by one equipment manufacturer to improve tool-to-tool reproducibility, a collaboration with a manufacturer in wafer temperature measurements, and the web-based NIST electron interactions database which distributes fundamental data to plasma modelers in industry and academia world-wide.

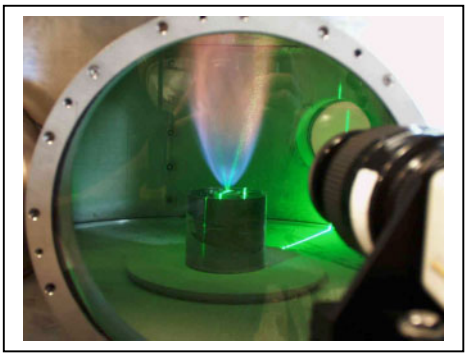
Future Plans: Future plans include obtaining maps of gas temperature in plasmas from PLIF measurements of the relative populations of several CF rotational levels, the further development of model-based process monitoring techniques, and adapting our plasma reactors to operate in the dual-frequency capacitively coupled mode used in state-of-the-art, industrial oxide etchers.

Measurement Technology for Benchmark Spray Combustion Data

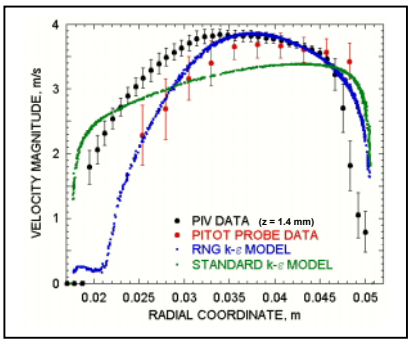
CSTL Program: Process Metrology
Authors: *C. Presser; J.D. Widmann (866); S.D. Leigh (898); D.S. Crocker (CFD Res. Corp.); and G. Papadopoulos (Dantec)*

Abstract: Control of process efficiency and the formation of species byproducts from industrial combustion systems (*e.g.*, power generation and treatment of liquid chemical wastes), relies increasingly on computational fluid dynamics (CFD) simulations to provide relevant process information in a cost-effective manner. However, reliable data for specifying model initial/boundary conditions is sparse. Therefore, there is a need for experimental/numerical comparative analysis of conditions within the reactor. Experimental data were obtained for the purpose of validating multiphase combustion models and submodels. A spray combustion facility was fabricated to permit well-defined input and boundary conditions, enabling measurements to characterize the fuel spray, combustion air, wall temperatures, gas temperatures, and species concentrations. The characteristics (i.e., size, velocity, volume flux, etc.) of the methanol fuel spray were determined using phase Doppler interferometry. Fourier transform infrared spectroscopy was used to measure the species concentrations in the reactor emissions, and the conversion of methanol in the reactor. Thermocouple measurements provide gas temperature data at the reactor exit. Particle image velocimetry was used to characterize the inlet combustion air, and also to provide validation data farther downstream.

Purpose: Develop measurement technology to provide benchmark experimental data for input/validation of multiphase combustion models, calibration of instruments/sensors, and development of advanced diagnostics. Such combustion process information forms the basis for investigation of particulate matter (PM) formation mechanisms. Collection of PM samples formed under well characterized conditions also provides the basis studying the dependence of PM characteristics on combustion condition.



Major Accomplishments: Experimental data were obtained for the purpose of validating multiphase combustion models and submodels. The NIST spray combustion facility (see top figure) provides well-defined input and boundary conditions, enables measurements to characterize the fuel spray, combustion air, wall temperatures, gas temperatures, and species concentrations. The characteristics (i.e., size, velocity, volume flux, etc.) of the methanol fuel spray were determined using phase Doppler interferometry. Fourier transform infrared spectroscopy was used to measure the species concentrations in the reactor emissions, and the conversion of methanol in the reactor. Thermocouple measurements provide gas temperature data at the reactor exit. Particle image velocimetry was used to characterize the inlet combustion air (see bottom figure), and also to provide validation data farther downstream.



Impact: This database is being used (and is available for future use) by several modeling groups for validation of multiphase combustion models.

Future Plans: This activity will be redirected to develop a suite of reproducible carbon-based particulate matter (PM) reference materials with properties approximating that of PM normally found in the environment.

International Comparisons of Temperature and Humidity

CSTL Program: International Measurement Standards
Authors: *D.C. Ripple, C.W. Meyer, G.F. Strouse, W.L. Tew, C.D. Vaughn, and B.W. Mangum (Guest Researcher)*

Abstract: The participation in international Key Comparisons is mandatory for a signatory National Measurement Institute (NMI) in the Mutual Recognition Arrangement (MRA) and acceptance of the MRA's Key Comparison Database (Appendix B). The results of the Key Comparisons are to be used to support the calibration and measurement capabilities [(CMCs), Appendix C] claims of each NMI; these Appendices produce the Key Comparison Database. In order to fulfill the requirements of the MRA, the NIST Thermometry Group is involved in four Comité Consultatif de Thermométrie (CCT) Key Comparisons in thermometry, one CCT Key Comparison in humidity, two preliminary SIM comparisons, and a bilateral comparison with NRC (Canada). The CCT thermometry comparisons are nearing completion, with CCT-K2 (13.8 K to 273.16 K) complete, CCT-K3 (83.8 K to 933.5 K) to be complete in early FY02, and the report for CCT-K4 (933.5 K to 1234.9 K) in progress. NIST was the pilot of CCT-K3 and the sub-pilot laboratory for CCT-K4. In order to prepare SIM NMIs for an extension of CCT-K3, two preliminary comparisons were started. NIST also led the effort to develop a protocol for a Key Comparison of humidity standards.

Purpose: The participation in Key Comparisons is mandatory for a signatory National Measurement Institute (NMI) in the Mutual Recognition Arrangement (MRA). The results of the Key Comparisons (Appendix B) are to be used to support the calibration and measurement capabilities [(CMCs), Appendix C] claims of each NMI. In turn, the validation of CMC claims is vital for international acceptance of NMI calibration services to customers and the resultant facilitation of global trade. In addition to the Key Comparisons, Supplemental Comparisons are useful to further support the CMCs and to explore technical issues that arise in the Key Comparisons.

Major Accomplishments: In FY01, the NIST Thermometry Group was active as the pilot of CCT-K3 (83.8 K to 933.5 K), as a participant in CCT-K2 (13.8 K to 273.16 K), and as a sub-pilot for CCT-K4 (933.5 K to 1234.9 K). Unanimous approval by the CCT was attained for the CCT-K2 Final Report and Appendix B and for the CCT-K3 Final Report. Results for CCT-K2 are now available on the BIPM Key Comparison Database (KCDB) website (http://kcdb.bipm.fr/BIPM-KCDB/). The CCT-K4 Report is currently a working draft and is awaiting approval by the participants before submission to the CCT. Within SIM, NIST initiated two SIM preliminary comparisons that are designed to be equivalent to CCT-K3. To verify the results of CCT-K3, a bilateral comparison was undertaken with NRC in the range 234.3156 K to 692.677 K. The measurements and a draft report for this comparison were completed. In the area of humidity, the NIST Thermometry Group led the task group that drafted a protocol for a Key Comparison of dew-point temperature.

Impact: Key comparisons establish levels equivalence of national measurement standards. KC results are maintained in the BIPM Key Comparison database. This equivalence, together with traceability within a nation to a single NMI, will promote the acceptability of measurements

across national boundaries, thereby minimizing measurement-based barriers to international trade.

Future Plans: In thermometry, Key Comparison work at the CCT level is nearing completion, with a draft of the CCT-K1 Report and completion and approval of Appendix B submissions for CCT-K3 and CCT-K4 all expected in FY02. The Thermometry Group will be focusing on the ongoing measurement phase of the SIM preliminary comparisons, and on publication of the results of the bilateral comparison with NRC. In humidity, the NIST Thermometry Group has responsibilities as Chair of the CCT Working Group on Humidity and will participate in a CCT-K6 comparison of dew-point temperatures, which is planned to start in FY02.

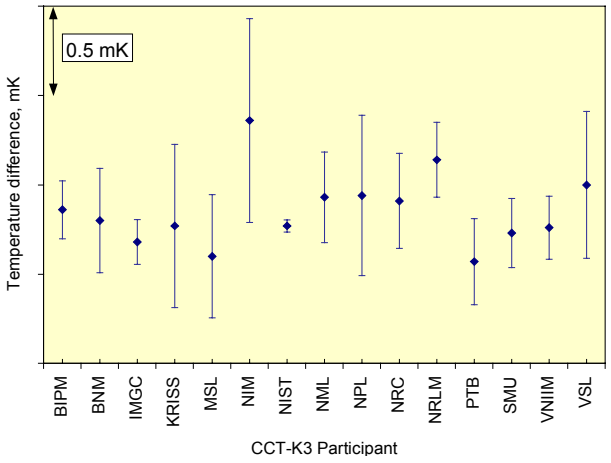


Figure 2. Differences in the realizations of the Ga freezing point, measured in CCT Key Comparison 3.

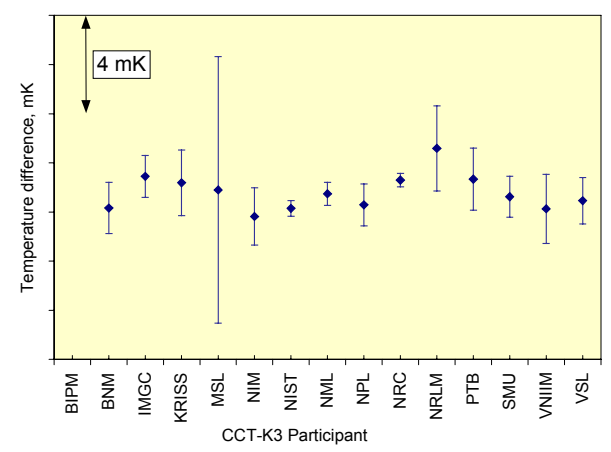


Figure 2. Differences in the realizations of the Zn freezing point, measured in CCT Key Comparison 3.

International Comparisons of Pressure Standards

CSTL Program: International Measurement Standards
Authors: *A.P. Miiller, D.A. Olson, R.G. Driver, P.J. Abbott, J.P. Looney, and A. Lee; T. Kobata (National Metrology Institute of Japan); and A.A. Eltawil (National Institute of Standards, Egypt)*

Abstract: The status of NIST participation in the CIPM international comparisons of pressure and vacuum standards is presented. In accord with the Mutual Recognition Arrangement (MRA), these comparisons help establish the level of equivalence of national standards between $3x10^{-6}$ Pa and 500 MPa. In FY01, NIST participated in four Consultative Committee for Mass and Related Quantities (CCM) Key Comparisons (KCs) and piloted three of them (two to completion of Draft B reports). These two completed comparisons were notable for being the first successful international comparisons in this pressure range (due to an innovative, NIST-developed, transfer standard design), and the only CCM pressure comparisons to be completed on-time. We also participated in a SIM comparison to 100 MPa, a bilateral comparison with Japan to 200 MPa, and a trilateral comparison with Japan and Egypt to 200 MPa. In all comparisons thus far, NIST is generally equivalent with other NMIs within our combined and stated uncertainties. In FY2002, measurements for all CCM KCs in pressure will be completed, but efforts will be placed toward supplementary SIM comparisons.

Purpose: Conform with the MRA in establishing the equivalence among the world's NMIs of pressure and vacuum standards for pressures between $3x10^{-6}$ Pa and 500 MPa. International trade is, in part, based upon the equivalence of national measurement standards. 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*	Participant NMIs*
CCM.P-K1.a, b	0.05 - 1 MPa (gauge)	Piston Gauge	Approved	a-6 b-3	1ab, 2a, 3ab, 5ab, 6ab
CCM.P-K1.c	0.08 - 7 MPa (gauge)	Piston Gauge	Approved	3	1, 2, 3, 4, 5, 6
CCM.P-K2	10 – 120 kPa (absolute)	Piston Gauge	In process	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	In process	1	1, 2, 5, 7, 8, 9
CCM.P-K4	1 - 1000 Pa (absolute)	Low Pressure Transducers	Draft B Complete	1	1, 2, 5, 7, 8, 9, 10
CCM.P-K5	1 – 1000 Pa (differential)	Low Pressure Transducers	Draft B Complete	1	1, 2, 5, 10, 11
CCM.P-K6	10 – 120 kPa (differential)	Piston Gauge	In process	2	1, 2, 5, 6, 10, 13, 14, 15, 16, 17, 18

Comparison CCM.P-K4 involved seven NMIs using two different principal techniques (liquid-column manometers vs. static expansion systems), and CCM.P-K5 involved four NMIs using two principal techniques (liquid-column manometers vs. double pressure balances). These comparisons, both piloted by NIST, encompass low to medium vacuum measurements, and are also important for accurate metering of low-speed air flows and altimetry. Participants completed measurements in FY99, and Draft B reports were completed in late FY01. Participating NMIs were generally equivalent (see figures), with some exceptions, and there did not appear to be any significant relative bias between the principal techniques. These two comparisons were also notable for being the first successful international comparisons in this pressure range (due to an innovative transfer standard design incorporating state-of-the-art MEMS-based sensors with traditional vacuum gauges), and the only CCM pressure comparisons to be completed on-time.

Comparison CCM.P-K3 is also piloted by NIST. The transfer-standard package that was developed by NIST consists of two spinning rotor gauges, three Bayard-Alpert ionization gauges, and began circulation in FY99. The comparison is 16 months behind due to delays between participants, but measurements should conclude in FY02.

In FY01, we also participated in a CENAM-led SIM comparison to 100 MPa, a bilateral comparison with Japan to 200 MPa, and a trilateral comparison with Japan and Egypt, also to 200 MPa. The results demonstrated general agreement between the participants and details can be found in the cited publications.

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 is the first successful comparison in this range, and was enabled based on integration of new MEMS-based sensors into the transfer package.

Future Plans: All six CCM-level Key Comparisons in pressure and vacuum are already finished, or will conclude their measurement phase in FY2002. In the coming year, we still must pilot CCM.P-K3 to conclusion, which includes data analysis and report writing. In addition, as NIST is the only SIM participant in all six CCM comparisons (with the exception of Canada in CCM.P-K2 and K6), we will necessarily be heavily involved in regional comparisons whose completion will provide other SIM countries with comparison results that can be entered in the Key Comparison Database. Also, based on strong customer demand from secondary calibration laboratories, we shall launch a new domestic comparison, under NCSLI auspices, in gaseous leak-rate measurement.

Publications:

J.C. Torres-Guzman, B.S. Cardona, and P.R. Couto, *Pressure Standards Comparison Within the Interamerican Metrology System (SIM), Up to 100 MPa*, NCSL International Workshop and Symposium, Washington, DC, Session 3D, July, 2001.

T. Kobata, J. W. Schmidt, and D. A. Olson, *Characterization of a High Pressure Controlled-Clearance Gauge*, submitted to The Society of Instrument and Control Engineers (Japanese domestic society)

T. Kobata, D.A. Olson, A.A. Eltawil, and A. Yonenaga, *Comparison of Working Pressure Standards in the Range Up to 200 MPa*, submitted to the Second Pressure Metrology Workshop, New Delhi, India, November 2001.

D.A. Olson, *Capabilities and Uncertainties of the Piston Gage Pressure Standards at NIST*, submitted to the Second Pressure Metrology Workshop, New Delhi, India, November 2001.

*Legend of NMIs:

1 National Institute of Standards and Technology (NIST) – United States
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) – South 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

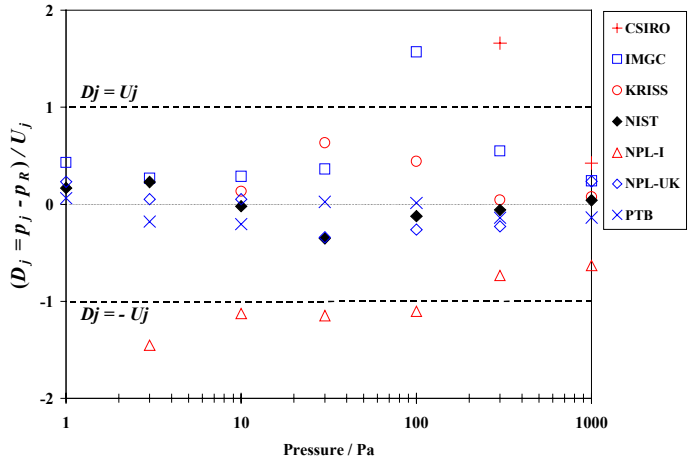


Figure 1. Results for CCM.P-K4: the deviation of National Metrology Institute *j* from the reference value divided by the uncertainty of this deviation (at a 95% level of confidence).

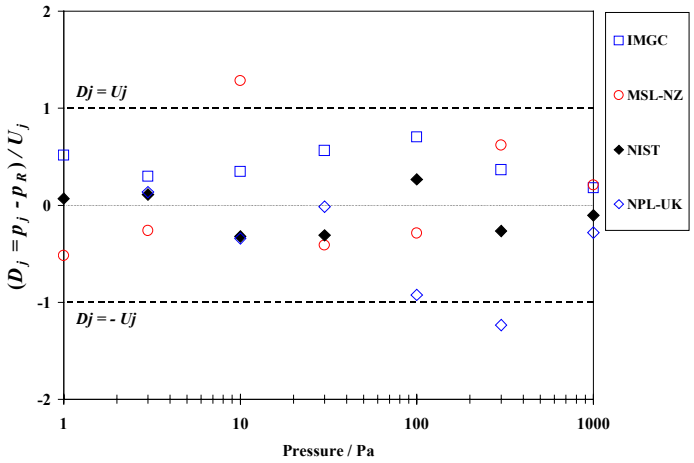


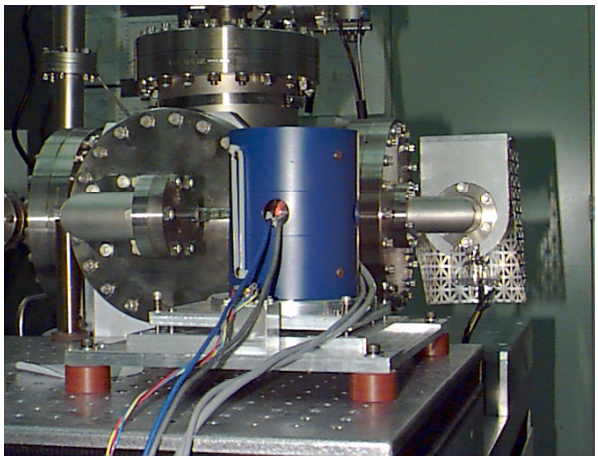
Figure 2. Results for CCM.P-K5: the deviation of National Metrology Institute *j* from the reference value divided by the uncertainty of this deviation (at a 95% level of confidence).

Improved Vacuum Transfer Standards

CSTL Program: Process Metrology
Authors: *J.P. Looney, R.F. Chang, P.J. Abbott, and A. Lee*

Abstract: Our ultimate goal is to disseminate NIST's realization of the Pa at ultrahigh vacuum levels directly to our customers and into readily available commercial gauges. While we offer precision calibration services, existing ultrahigh vacuum gauges are so unstable that it is a challenge to effectively disseminate NIST's uncertainties into practical industrial and secondary calibration settings. Our efforts, in the near term, focus on improving our calibration services. In the long term, we will develop a compact, chemically inert, robust high vacuum gauge, based on the spinning rotor gauge (SRG), with excellent stability (<0.5% shift in calibration per year) and precision, that can operate from 10^{-7} to 1 Pa. This will effectively disseminate NIST's realization of the Pa, along with our low uncertainties, directly to our customers, and will enable precision vacuum processing and control applications, as well as the transfer standards necessary to conduct meaningful international comparisons of vacuum standards. The main challenge of this project is to extend the capabilities of the SRG, which currently functions to the 10^{-4} Pa, to lower pressures.

Purpose: The spinning rotor gauge (SRG) has become the transfer standard of choice for vacuum calibrations from 10^{-4} Pa to 1 Pa due to excellent calibration stability (changes < 0.5%/year), high precision, and inertness to process gases. Current technical constraints limit SRGs to pressures above 10^{-4} Pa. Below 10^{-4} Pa, stable transfer standards are not available, leaving hot-cathode ionization gauges as the primary alternative. However, ion gauge reactivity with many gases and their notorious instability (changes >5-10%/year) are important drawbacks. Their large instability/uncertainty, often an order of magnitude larger than national primary standards, cause problems in establishing degrees of equivalence and mutual recognition of calibration certificates via intercomparisons. Further, ion gauge and SRG calibrations are time consuming, labor intensive, and expensive. Greater efficiencies in the calibration services are sought, including ways to speed turnaround time and introduce a greater level of automation.



Spinning Rotor Gauge with Low-Friction Suspension System

Major Accomplishments: Many improvements have been, and are being made to NIST's ion gauge and SRG calibration services. A new flowmeter has been designed to overcome problems with the previous generation device, achieve smaller uncertainties in our primary ultrahigh and midrange vacuum standards, and increase overall system reliability. We also added a pre-calibration instrument check to our ion gauge calibration service to weed-out malfunctioning gauges, which would otherwise slow the data acquisition and review activities of the our calibra-

tion process. We also quantified effects of baked versus non-baked SRG rotors and thimbles, and we have assessed the effects of "gradually" versus "suddenly unsuspended" rotors. These are important effects to quantify as we look for ways to improve customer utilization of calibrated SRGs, recognizing that many customers do not bake their devices and may not carefully spin-down their rotors.

To extend the operating range of the SRG, we must address four challenges: 1) Adapt state-of-the-art frequency measurement technology to our timing measurements; 2) Develop very low friction (or residual torque) magnetic suspension systems; 3) Thermally stabilize the SRG to minimize thermal variations which give rise to a 'fictitious' torque; and 4) Isolate the SRG head from external vibration. We have demonstrated the feasibility of improved frequency measurements, and are now incorporating low-noise componentry into the controlling electronics. A prototype low-friction suspension system has been provided by the original SRG developers at the *Forschungszentrum Jülich*, Germany and has been used successfully (see figure).

Impact: The current improvements to our high vacuum calibration services have already reduced costs to some ion gauge customers.

Future Plans: We shall investigate the feasibility of an on-demand SRG calibration service. Evidence suggests that we can offer this service, with little degradation in overall uncertainty, but speed-up turnaround from months to days. We shall begin testing of the prototype SRG which will incorporate low-noise electronics and low-friction suspension system. Vibration isolation and temperature stabilization experiments will also be subsequently performed. We expect to define the limits of operation and performance of this new device in FY02.

Chemical Microsensors

CSTL Programs: Chemical and Biochemical Sensing (also Environmental Measurements, Nanotechnology)
Authors: *S. Semancik, R.E. Cavicchi, N.O. Savage, C.J. Taylor, C.B. Montgomery, M.C. Wheeler, M. Carrier, and J. Melvin*

Abstract: This project on solid state microsensor research is motivated by the increasing need for reliable, rapid, low cost measurements of the chemical composition in the gas phase. Efforts have been directed toward development of advanced MEMS-based (low power consumption) measurement platforms, thin film sensing materials, and fundamental detection concepts for application-tunable measurement technology. Core program studies seek to move the field forward by examining fundamental measurement issues, such as control of film nanostructures for higher sensitivity and rapid adsorption/desorption transient behavior at sensor surfaces to create analyte-specific signatures. The performance of device prototypes for certain application sectors is also investigated. Work supported by the Environmental Management Science Program of DoE led to the development of a database of sensing materials and operating conditions for the detection of hazardous chemicals at nuclear waste sites. A DTRA (Defense Threat Reduction Agency) sponsored task demonstrated the detection of trace amounts of simulants for mustard and nerve agents. A new task, supported by NASA, will study the applicability of NIST microsensors for trace analyte detection in planetary atmospheres. These activities aim to accelerate the development of chemical and biochemical micromeasurement systems for environmental, defense, and health related applications.

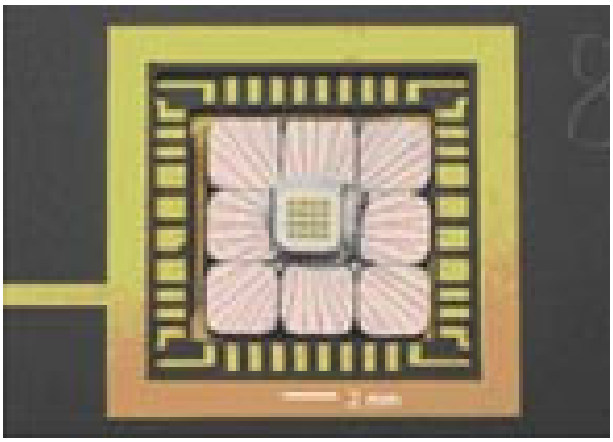


Figure 1. 16 element micro-sensor array mounted in a 40 pin package.

Purpose: This project addresses the basic scientific and measurement science issues associated with using chemical microsensors in applications such as environmental monitoring, process control, and personal safety. Fundamental areas studied include: 1) design of generic and flexible microsensor platforms using MEMS technology, 2) development of more stable and sensitive sensing materials, 3) elucidation of transduction mechanisms as a basis for improvement in operation and performance, 4) development of data analysis models for extracting quantitative chemical information from nonlinear signals. Microsensors are tuned for specific analytes by using arrays that contain elements with varied sensing materials and/or by using temperature programming capabilities of microsensor platforms to provide unique electronic signatures. The microsensor's exceptional tunability permits application to varied chemical analysis problems, including chemical waste monitoring and remediation (DoE), detection of chemical warfare agents (DTRA), exploration of planetary atmospheres (NASA), and sensing of fuel cell feedstocks (ATP).

Major Accomplishments: A variety of core NIST program and other agency chemical measurement objectives were realized in FY01.

- Detection of simulant molecules of chemical warfare agents in the 1 ppm range, and the demonstration of recognition effects based on temperature-dependent reversal of the conductance response polarity (DTRA)
- Demonstration that chemometric signal processing methods properly separate and quantify mixed analytes for microsensor data
- Established in-house MEMS design capabilities and completed new design set for improved microsensor platforms.
- Demonstration of microarray-based parallel studies of 36 microsamples, for efficiently producing a database on the response characteristics of varied sensing materials to a suite of six hydrocarbon gases/vapors (DoE)
- Demonstration of a microscale temperature pulsing technique which utilizes MEMS structures to determine kinetic parameters for adsorption and desorption phenomena

Impact: With the detection of low concentrations of simulant molecules, field tests of actual nerve agents at Army laboratory facilities are anticipated in late 2001. These studies will help determine whether microhotplate sensors can become a tool in the counterterrorism arsenal. The ability to recognize a number of analytes of interest at DoE nuclear waste sites is expected to lead to DoE field tests in 2002 to evaluate microsensor performance in monitoring subsurface hazardous chemicals. The patented microsensor technology has also been disseminated to several companies and research groups. Boston MicroSystems is developing a SiC version of the NIST microhotplate for varied sensing applications under a CRADA. NIST Research Licenses were issued to Cyrano Sciences and the University of Massachusetts to study the suitability of microsensor platforms for electronic nose and explosives detection applications, respectively. A NASA supported project with Cal Tech/Jet Propulsion Laboratory researchers was also initiated to develop microarray measurement systems that include both oxide and polymer sensing films.

Future Plans: Research will continue on developing sensing interfaces with improved sensitivity and stability for operation in gases and vapors. We will also investigate methods for faster generation of sufficiently dense sensing data for application areas that require rapid analyses (less than ~ 5 sec). Efforts will also be directed toward developing MEMS-based calorimetric sensors, functional materials for integrated filters and preconcentrators, and incorporating microsensors in microfluidic devices for complete integrated chemical and biochemical analysis systems.

BioMEMS Measurement Systems

CSTL Program: Chem/Bio Sensing
Authors: *T.H. Huang, R.E. Cavicchi, and M.J. Tarlov; and S. Stranick (837)*

Abstract: The goal of this project is to accelerate the merging of biological systems with silicon micromachined technology to develop selective, ultrasensitive, miniaturized chemical and biochemical measurement tools. These new tools, so-called BioMEMS devices, hold tremendous promise for point-of-care health care measurements and for rapid detection of potential bioterrorism pathogens. Major scientific and technical challenges to be overcome include 1) developing robust, self-assembly-based protocols, with submicrometer resolution, for directing and attaching biological molecules to MEMS structures; 2) developing analytical techniques for characterizing the activity of biological/MEMS structures; 3) ensuring compatibility of MEMS devices with aqueous biological environments; and 4) developing novel MEMS-based transduction strategies for detecting biological recognition events. Research is focussed on a model, prototypical BioMEMS device and reaction: the melting of DNA on microhotplate (μHP) devices. The heat producing and temperature measurement capabilities of μHPs hold great promise for monitoring and detecting biological reactions. The major accomplishments this year include: 1) selectively attachment of single-stranded DNA probes to gold-coated microhotplate surfaces, 2) verification with fluorescence microscopy of biological activity of the immobilized probes by hybridization with complementary DNA 3), and denaturation, or melting, of the surface confined hybrids using heat generated by the microhotplate device.

Purpose: The goal of this project is to accelerate the merging of biological systems with silicon micromachined technology to develop selective, ultrasensitive, miniaturized chemical and biochemical measurement tools. These new tools, so-called BioMEMS devices, hold tremendous promise for point-of-care health care measurements and for rapid detection of potential bioterrorism pathogens. In realizing this goal, however, major technical challenges must be overcome. These problems include 1) developing robust, self-assembly-based protocols, with submicrometer resolution, for directing and attaching biological molecules to MEMS structures; 2) developing analytical techniques for characterizing the activity of biological/MEMS structures; 3) ensuring compatibility of MEMS devices with aqueous biological environments; and 4) developing novel MEMS-based transduction strategies for detecting biological recognition events.

Major Accomplishments: In the first year of this project our efforts have focussed on a model, prototypical BioMEMS device and reaction: the melting of DNA on microhotplate (μHP) devices. This particular BioMEMS system was chosen for investigations for two primary reasons. First, it leverages existing expertise in design, fabrication, and metrology of μHP devices, and self-assembly and measurements of surface-confined DNA. Secondly, temperature-based measurements of biological systems hold great promise for monitoring and detecting biological reactions. The μHPs are sensitive devices for effecting and measuring temperature changes, and may potentially serve as generic measurement platforms for a variety of BioMEMS applications. The major accomplishments this year include: 1) selectively attachment of single-stranded DNA probes to gold-coated microhotplate surfaces, 2) verification with fluorescence microscopy of biological activity of the immobilized probes by hybridization with complementary DNA 3), and melting of surface-confined hybrids using heat generated by μHP devices (see Figure).

Impact: The measurements, self-assembly protocols, and biological/silicon integration methods developed in the BioMEMS project are expected to be broadly applicable to different BioMEMS devices. We will reach customers, primarily micro-device-oriented biotechnology and MEMS start-ups, through publications, patents, and direct collaboration. Several biotechnology companies have already indicated interest in integrating biochemical assay protocols with μHP platforms for genetic diagnostics and immunoassays, however, these companies lack in-house expertise and measurement facilities for adapting established biological protocols with MEMS structures.

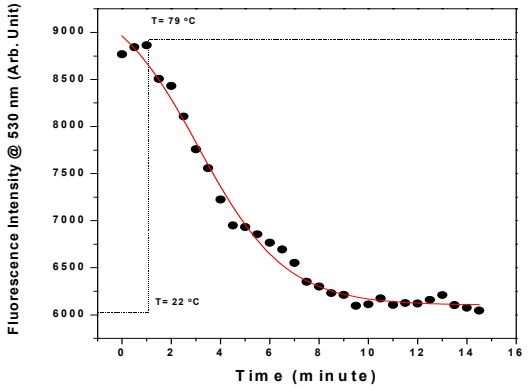


Figure 1. Melting curve

Future Plans: Future plans include kinetic measurements of DNA melting from μHPs to determine if information concerning base-pair mismatches can be extracted from data. Reliable and accurate determination of DNA mismatches, or so-called single nucleotide polymorphisms (SNPs) are expected to form the basis of many health-care related genetic assays. In addition, we plan to exploit the individually addressable heating capabilities of the μHPs to develop protocols for selective deposition of DNA sequences, a capability that would allow for DNA array-based applications.

Research Toward Developing an Absolute Pressure Standard

CSTL Program: Process Metrology
Authors: *M.R. Moldover, and J.W. Schmidt; and K. Szalewicz (U. Delaware)*

Abstract: Development of a novel, primary, standard for pressure in the range 0.3 MPa – 5 Mpa is planned. This will be accomplished by measuring and calculating the dielectric constant $\varepsilon(p,T)$ of helium with extraordinary accuracy. When this is achieved, the determination of the pressure $p(\varepsilon,T)$ from electrical and temperature measurements will have a smaller uncertainty than the determination of pressure using existing 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.

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 figure 1.) We measured C_{TB} and C_{IO} and computed their average: $C_x = (C_{TB} + C_{IO})/2$, which is the cross capacitance. The average compensates for relative motion of the electrodes (changes in s in figure 1) and for dielectric layers on the electrode surfaces, such as oxides, adsorbed water, or films of oil. During use, the cross capacitor is enclosed by a pressure vessel that is filled with the gases under test.

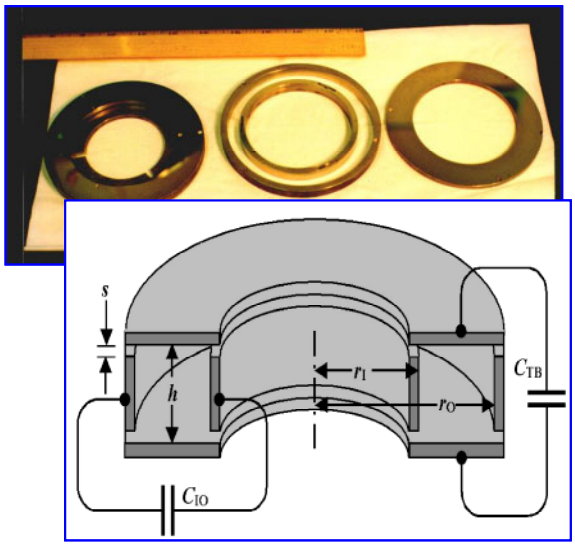


Figure 1. Toroidal cross capacitor and components.

During FY01, the cross capacitor and pressure vessel were tested at 0°C and at 30°C by measuring the dielectric constant of helium. Earlier tests had been made at 50°C. All of the measured values of $\varepsilon(p,T)$ were consistent with the theoretical values. However, the uncertainty of comparison was not limited by the uncertainty of the pressure measurement. Instead, it was limited by the uncertainty of the capacitance measurements that were made

measurements that were made using the most accurate, commercially manufactured, capacitance bridge.

During FY01 improvement in the quantum-mechanical calculation of the molar polarizability of helium were made by Szalewicz.

$$A_\varepsilon \equiv \lim_{p\to 0}\left[(\varepsilon(p)-1)/\left((\varepsilon(p)+2)\rho(p,T)\right)\right].$$ (Here $\rho(p,T)$ is the molar density.)

Szalewicz's value of A_ε is identical with the value of A_ε obtained independently by a group at Notre Dame, within the estimated relative uncertainty of 2×10^{-6}. This uncertainty would be the relative uncertainty of the pressure standard if the measurements of $\varepsilon(p,T)$ were perfect and if the density virial coefficients of helium were sufficiently well know. Szalewicz is now improving the calculations of the density virial coefficients.

During FY01, the cross capacitor system was used to measure dielectric constants of the primary constituents of natural gas (methane, nitrogen, carbon dioxide, and argon) at 30ºC and at 0ºC to provide reference data for use in metering natural gas. These data supplement the reference data previously acquired at 50ºC and recently published. [Moldover, M.R., and Buckley, T.J., Reference Values of the Dielectric Constant of Natural Gas Components Determined with a Cross Capacitor, Int. J. Thermophysics, Vol. 22, pp. 859-885 (2001).]

Impact: Successful conclusion of this research effort will result in a completely new approach to realization of the unit of pressure that has the potential to reduce measurement uncertainty below that ultimately achievable with current piston gauge technology. As is not the case with high accuracy thermometry, high accuracy electrical metrology will be needed to support this effort.

Future Plans: Improvements in electrical metrology are needed. Two routes to improved capacitance measurements will be pursued: (1) design, manufacture and calibrate a special-purpose capacitance bridge optimized for the specific measurements needed, and (2) design and manufacture a cross capacitor with a much larger capacitance than the 0.5 pF value of the prototype shown in Figure 1.