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Development of a New NIST Calibration Service Using the Comparison Method for Vacuum Gauges Spanning the Range 0.65 Pa to 133 kPa

Authors: *Jay H. Hendricks and Patrick J. Abbott, Jacob E. Ricker and Justin H. Chow, Jeffrey D. Kelley (Div. 836)*

Program Identification: Industrial and Analytical Instruments and Services

Context: Many NIST customers using our vacuum calibration services spanning the pressure range from 0.65 Pa to 133 kPa (5 millitorr to 1000 torr) desire direct traceability to NIST but cannot justify the cost of calibration against relative to the NIST NIST Ultrasonic Interferometer Manometers (UIMs). These customers are typically using less accurate gauges, such as Thermal Conductivity Gauges[1-2] (TCGs), or the newer combination type gauges that have 2 sensors combined with an electronic processor that averages or selects which sensor is being utilized depending on the pressure being sensed. A new calibration service based on a secondary pressure transfer standard spanning this pressure range is being developed at NIST. It is designed to add a lower accuracy level service consistent with the needs of these customers and will follow a model where a less accurate, and less costly, service is offered to customers who do not require the lowest uncertainty available from NIST.

Introduction: The Comparison Method Vacuum Gauge calibration service under development at NIST has been designed with the NIST calibration customer in mind. From the onset, the goals for this project were to reduce turn-around-time, calibration cost, and to provide an on-demand vacuum gauge calibration service. This new services is aimed at a class of pressure instruments whose accuracy capabilities are significantly less than that of the NIST standards currently used for calibration. Use of calibration standards consistent with the performance capabilities of this instrument class and utilizing extensive computer automation as part of the design conceptconsists of:

- A high-stability Transfer Standard Package (TSP) that provides traceability to NIST primary pressure standards and
- An automated test stand where the high-stability TSP and customer gauges can be compared with a series of computer-controlled pressure test points spanning the barometric pressure range of 0.65 Pa to 130 kPa.

At the core of the Comparison Method Vacuum Gauge calibration service is a NIST-designed, built, and tested TSP, consisting of two different gauge technologies: Resonant Silicon Gauges (RSGs) and Capacitance Diaphragm Gauges (CDGs). The RSG technology has demonstrated superior long-term stability (drifting less than 0.01% per year) while the long-proven CDG technology provides superior low-pressure resolution at pressures below 133 Pa (1 torr). High-stability TSPs have been periodically calibrated against the NIST 160 kPa UIM and 140 Pa Oil UIM Primary Pressure Standards as part of our efforts in demonstrating the equivalence of NIST pressure standards relative to those of other nations. This TSP design has demonstrated excellent long-term accuracy with a considerable degree of robustness.

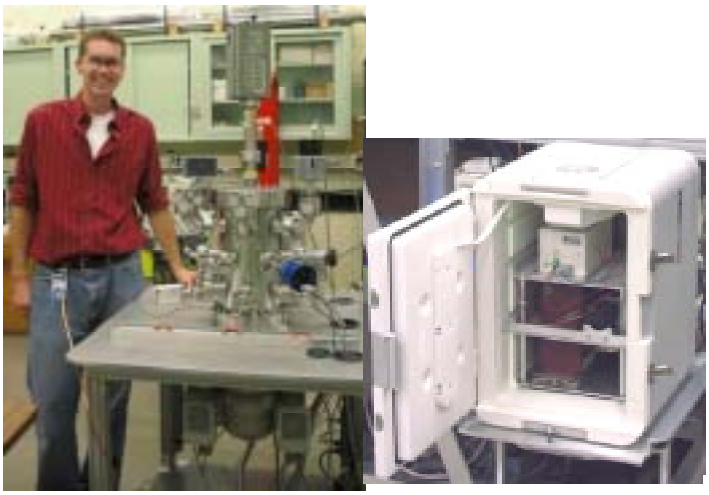
The automated test stand has been developed using vacuum technology that will enable computer control of calibration fill pressures and data acquisition. Fill pressures spanning the range of 0.65 Pa to 133 kPa will be controlled with a combination of a throttling gate valve (TGV) and a mass flow controller (MFC). The TGV and MFC are easily computer controlled enabling

automation of calibration gas fill pressures. A Residual Gas Analyzer (RGA) mounted on the test chamber will enable rapid and leak-testing of customer gauges for quality control.

Impact: The Comparison Method Vacuum Gauge calibration service will meet the needs of NSIT customers who require direct NIST traceability, reduce NIST vacuum gauge calibration cost and turn-around-time, while providing on-demand vacuum gauge calibration services. This new service will offer service to customers who do not require the lowest uncertainty possible, enabling them to obtain a NIST calibration of less accurate vacuum gauges not currently calibrated at NIST, including TCGs, and new combination gauges employing multiple sensor technologies (TC, CDG, Piezoresistive, and RSG). The Comparison Method Vacuum Gauge Service is designed to have expanded uncertainties as low as 0.05 % from 1.33 kPa to 133 kPa (10 torr to 1000 torr) and 0.3 % from 1.33 Pa to 1.33 kPa (0.01 torr to 10 torr).

[1]R. E. Ellefson, A. P. Miiller, J. Vac. Sci. Technol. A 18(5) pp. 2568-2577, 2000.

[2]NIST Internal Calibration Report NC201



Left: Jacob Ricker standing next to the new NIST comparison method vacuum gauge calibration service test stand. Right: The high-stability Transfer Standard Package that provides direct traceability to the NIST 160 kPa and 140 Pa Primary Pressure Standards.

High Pressure Standards Based on Compact Piston Gauges

Authors: *Douglas Olson (836), A.K. Bandyopadhay (Guest Researcher)*

Program Identification: Industrial and Analytical Instruments and Services

Context: NIST provides world-class standards for pressure measurements through development of innovative approaches to realization of those standards. The purpose of the work described here is to determine the performance of piston/cylinder assemblies (i.e., piston gauges) operating at high pressures, thereby establishing their utility as primary pressure standards. The ultimate goal is to realize the unit of pressure, the pascal, and transfer the unit of pressure to our customers at the lowest uncertainty possible to satisfy customer needs in aviation, weather prediction, safety considerations affecting many industries using processes where pressure control and regulation and safety of containment structures are critical considerations in both design and operation.

Introduction

The accurate measurement of pressure is required for determining the altitude of aircraft, measuring barometric pressure for weather prediction, optimizing the performance of engines and industrial processes, and process control in manufacturing. At pressures ranging from atmospheric to very high pressures, piston gauges are used as primary and secondary pressure standards at National Metrology Institutes as the basis for national and international pressure scales. In the pneumatic region below 1 MPa, large diameter piston gauges supported with improved dimensional capability and manometric pressure standards make it possible to achieve a relative standard uncertainty in pressure of a few parts in 10^6. Uncertainties in the hydraulic pressure region can be significantly higher, in particular above 100 MPa. In the past, hydraulic piston gauge standards have used very large mass loads (400 kg or more). We have been studying the performance of a new generation of compact piston gauges that offer the potential for reduced uncertainties. The gauges have a smaller, integrated design, and use existing mass sets.

Recently, two US manufacturers have provided to NIST compact piston gauges of the "controlled-clearance" type. This class of piston gauges uses an auxiliary pressure to "control" the distortion of the cylinder element, which becomes significant above 10 atmospheres of pressure. The use of auxiliary pressure also allows establishing the gauge as an independent, primary standard. We have made extensive performance measurements of the first of these two piston gauges [1], which operates to 200 MPa. This gauge uses a common 100 kg mass set, is easily transportable, and is based on a commercial line of piston gauges with modern PC-based controls and protocols. The cylinder was designed for minimal vertical loading, which allows its experimental distortion to more closely match that from elasticity theory of solids deformation.

Major accomplishments

The compact piston gauge has shown excellent repeatability over a two-year period (relative agreement of 1.1×10^{-6} in the effective area). The gauge also agrees to the present NIST pressure scale to better than its standard uncertainty, with a maximum deviation of 22 ppm through NIST gauge PG21(xx MPa) and 33 ppm through NIST gauge PG479 (xx MPa). The figure shows the agreement between the effective area from the characterization equation [what's the characterization equation, 1st mention] and the area from direct comparison to the present NIST pressure scale.

Impact

The compact design of these piston gauges supports easy shipped to other installations and makes them excellent candidates for use as pressure transfer standards. For the first time, international comparisons can be contemplated using direct comparison of primary standards, rather than with a secondary transfer standard. Ease of use will also allow more frequent checks at NIST of the primary standard against NIST secondary standards, or perhaps direct calibration of customer gauges against the primary standard. [what's the "primary" in this discussion?]

Future plans

This year, NIST will begin studying the performance of the second of the two controlled clearance piston gauges from the US manufacturers. This gauge can operate to higher pressure (280 MPa vs 200 MPa), more closely matching the range of NIST secondary standards.

Outputs

"Characterization of a compact 200 MPa controlled clearance piston gauge as a primary pressure standard using the Heydemann and Welch method", A.K. Bandyopadhyay and D.A. Olson, *Metrologia* **43**, 573-582 (2006).

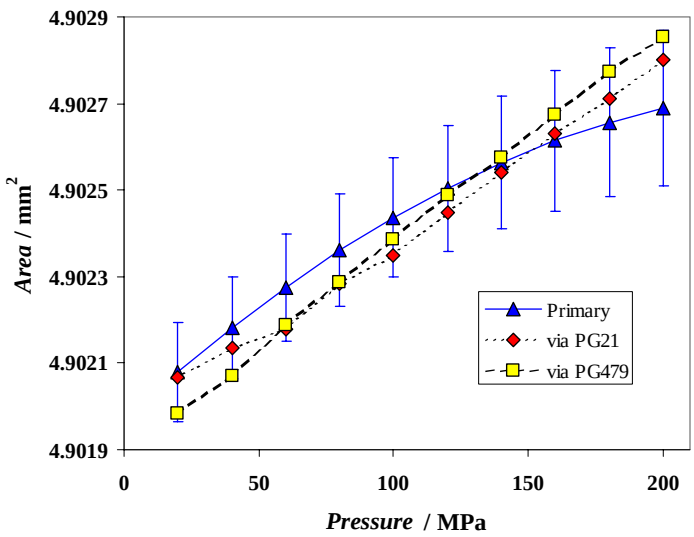


Figure 1. Comparison of the effective area from characterization method (Primary) that from the present NIST pressure scale (via PG21 and via PG479), for new compact controlled clearance piston gauge. Areas agree to within standard uncertainty of the compact gauge throughout the pressure

Reference Values of Gas Viscosity

Authors: *Michael R. Moldover, Eric F. May, (Guest Resercher), Robert F. Berg, John J. Hurly (836)*

Program Identification: Industrial and Analytical Instruments and Services

Context: The manufacturers of semiconductor devices and producers and consumers of natural gas rely upon accurate measurements of gas flow rates for equitable transfer in markets. The range of requirements differ by factors as large as 10^9. Improved gas flow rate measurements increase confidence in market transactions and are enabled by gas property data of improved accuracy. NIST has refined techniques to produce reference values for the viscosity and thermal conductivity of argon with a standard uncertainty of only 0.08 %. Prior methods provided such data with uncertainties of 0.xx%. The viscosity of hydrogen, methane, and xenon will be obtained with similarly small uncertainties. The low uncertainty of these results also advances the fundamental models of intermolecular potentials which has what effect???.

Introduction: We combined NIST's quantum mechanical calculations of the viscosity of helium [0,2] with measurements made with two, newly developed viscometers. One viscometer [3] used a coil of quartz capillary tubing of high uniform diameter. These are normally used for gas chromatography. During its operation, gas flows through the capillary, transducers measure the pressures at the entrance and exit, and a hydrodynamic model converts the pressure measurements to a flow rate value. The second viscometer [4] used two capillaries in a series configuration, one maintained at 25 °C, and the other at temperatures ranging from 200 K to 400 K. Important features of the two-capillary viscometer include (1) electro-formed nickel tubing with an extremely smooth internal surface, (2) voltage controlled piezoelectric leak valves, (3) pressure transducers maintained in thermostatically controlled enclosures, and (4) *in situ* calibration with helium at each temperature and time of use.

The two-capillary viscometer determined the ratio of the each gas's viscosity to that of helium, which is known with an. uncertainty smaller than 0.1 %. For the noble gases argon and xenon, the measured viscosities were combined with calculations of the Prandtl number to yield the thermal conductivities with uncertainties of 0.08 % [4].

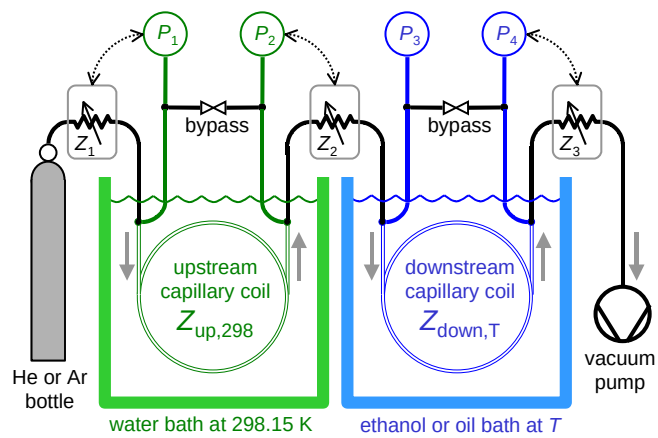


Figure 2. Schematic diagram of the two-capillary viscometer. The impedances Z_{up} and Z_{down} were coiled nickel capillaries with a length of 7 m and an inside diameter of 0.8 mm. The variable impedances Z_1 and Z_3 were piezoelectric gas leak valves and Z_2 was either a leak valve or a mass flow controller.

Both viscometers used a hydrodynamic model for capillary flow, also developed recently at NIST [5]. By incorporating the six most important corrections to the Hagen-Poiseuille equation for capillary gas flow, the model added negligible uncertainty to the final result.

Major accomplishments: The consistency of the measurements, and their agreement with the most accurate calculations of the viscosities of helium and argon, verified the accuracy of both viscometers. This improved measurement method has resulted in improvement in the accuracy of argon's thermal conductivity that is 30 times better than prior knowledge of this quantity. [6].

Impact:

- The reference values for viscosity and thermal conductivity will enable improvements of the thermal mass flow controllers that are used widely by the semiconductor industry.
- This technique will enable accurate measurements of the viscosity of natural gas components at process and pipeline conditions.
- This technique could be extended as a cost-effective flow method to produce reference quality gas mixtures.
- Further work based on this technique would improve the models of the fundamental interactions between molecules. Extending the measurements to high pressures would provide the accurate data needed to develop reliable models of three-body collisions.

Future plans: Analysis of the measurements of hydrogen, methane, and xenon is near completion and will form the basis for publication of the results.

References

1. "*Ab initio* values of the thermophysical properties of helium as standards", J. J. Hurly and M. R. Moldover, *J. Res. NIST* **105**, 667-688 (2000).
2. "Improved *ab initio* values of the thermophysical properties of helium as standards", J.J. Hurly, M.R. Moldover, and J.B. Mehl, presentation at *Sixteenth Symposium on Thermophysical Properties*, Boulder, CO (2006).
3. "Quartz capillary flow meter for gases", R.F. Berg, *Rev. Sci. Instrum.* **75**, 772-779 (2004).
4. "Transport properties of argon at zero density from viscosity-ratio measurements", E.F. May, M.R. Moldover, R.F. Berg, and J.J. Hurly, *Metrologia* **43**, 247-258 (2006).
5. "Simple flow meter and viscometer of high accuracy for gases", R.F. Berg, *Metrologia* **42**, 11-23 (2005) [erratum **43**, 183 (2006)].
6. E. W. Lemmon and R. T. Jacobsen, *Int. J. Thermophys.*, **25**, 21-69 (2004).

Metrological Shortcomings of Teflon-Based Helium Permeation Leak Artifacts

Authors: *Patrick J. Abbott and Justin H. Chow*

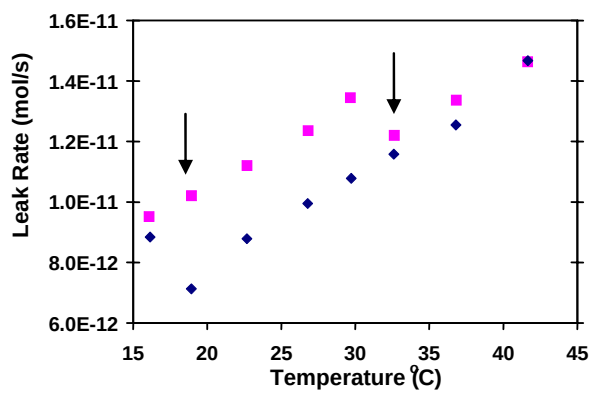
Program Identification: Industrial and Analytical Instruments and Services

Context: Accurate and non-destructive leak testing of sealed vessels is important in diverse industries, ranging from food packaging to nuclear waste containment. Common applications include the testing of process chambers that operate under vacuum conditions such as in the semiconductor and space simulation industries. In many cases, quantifying leak rates provides a "go/no-go" indicator of overall process health. In order to ensure consistent and accurate measurements, it is vital that leak testing equipment be calibrated with accurate transfer standards. The Leak Calibration Program at NIST calibrates helium permeation leak artifacts for customers who use the artifacts to calibrate mass spectrometer-based leak detectors used for a range of leak qualification applications.

Photo of a Teflon-element permeation leak artifact. The Teflon element is the white rod on the far right of the photo.

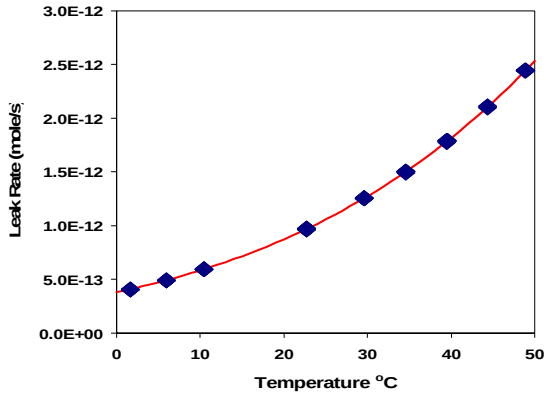
Leak artifacts consist of a containment vessel that is easily connected to the system of interest, generally using commonly used fittings. Recently it was discovered [how??] that certain types of helium leak artifacts that use Teflon™ as the leak element may have errors larger than their calibration uncertainties due to a temperature-induced phase change[1] within the Teflon. The figure below shows discontinuities near 19 ^{o}C and 30 ^{o}C in the calibration of such a device that amount to a 30 % change, which is nearly four times the manufacturer's stated uncertainty! In contrast, the behavior of a glass element helium permeation leak deviates by no more than a percent or two from a smooth exponential response with temperature.

Not all of the Teflon-based leaks tested at NIST showed the same extent of anomalous behavior with temperature, but alerting customers of the possibility of these types of errors should help in making the choice of a calibration artifact for a particular process uncertainty budget. Publication of these results is planned for an archival metrology journal (*Measure*).



Calibration of Leak Rate vs. Temperature for a typical Teflon-element helium permeation leak. The diamonds indicate ascending temperature, the squares indicate descending temperature. Note the discontinuities (arrows) at 19° and 30°

[1]Quinn Jr., Fred A., Roberts, Donald E., and Work, R. N., Journal of Applied Physics 22, 1085-1086 (1951)



Calibration of Leak Rate vs. Temperature for a typical glass-element helium permeation leak.

Characterization of Chemical and Biological Coatings on Au nanoparticles by Differential Mobility Analysis

Authors: *R. Zangmeister, L. Pease, M. Tarlov, D.-H. Tsai, and M. Zachariah*

CSTL Program: Technologies for Future Measurements and Standards (Tech)

Context: The National Cancer Institute (NCI) of the National Institutes of Health established the Nanotechnology Characterization Laboratory (NCL) to provide the critical infrastructure and characterization services to accelerate the development and application of nanoparticles and nano-devices for the diagnosis and treatment of cancer. Nanotechnology holds huge promise for the design and manufacture of many types of novel medical products—from devices to therapeutics to combination products. NIST is working closely with the NCI/NCL to develop standards, measurement methods, and protocols for the quantitative and reproducible characterization of nanoparticles. The focus of this project is to develop measurement techniques to characterize the physical size and chemical composition of organic and biological coatings of modified gold nanoparticles. Both the NIH and FDA have stated that an urgent measurement need is the development of novel methods to characterize the chemical or biological coatings on nanoparticle surfaces. These coatings play critical roles in fighting cancers because they frequently are designed as therapeutic or targeting agents.

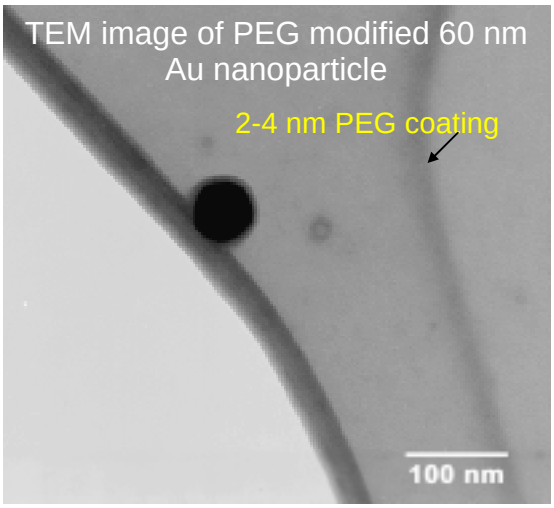
Approach: Our approach to characterize the surface coatings is to measure the nanoparticle size before and after surface modification. The difference in particle size provides an estimate of the coating thickness which can be used to deduce the molecular surface coverage of chemical or biological molecules. We use a novel gas phase method to measure nanoparticle size: electrospray ionization - differential mobility analysis (ESI-DMA). The primary advantage of the ESI-DMA is its excellent resolution, being able to discern particle size differences as small as 0.2 nm. To determine the utility of the ESI-DMA method for characterizing nanoparticle coatings we use a model system, Au nanoparticles modified with self-assembled monolayers (SAMs) of thiolated aliphatic molecules or DNA oligomers. The SAMs produce well-defined chemical coatings on commercially available gold nanoparticles with narrow size distributions. The particle size, d, is characterized based on the difference of electrical mobility, which is inverse proportional to the surface area of a particle. After successful coating process, the electrical mobility of the Au nanoparticle should be reduced due to the increased surface area of the particle due to the molecular coating. The functionalized Au nanoparticles are transferred from solution to the gas phase using electrospray particle generation where Au nanoparticles are carried by a CO_2/air gas flow and then delivered into the analyzer.

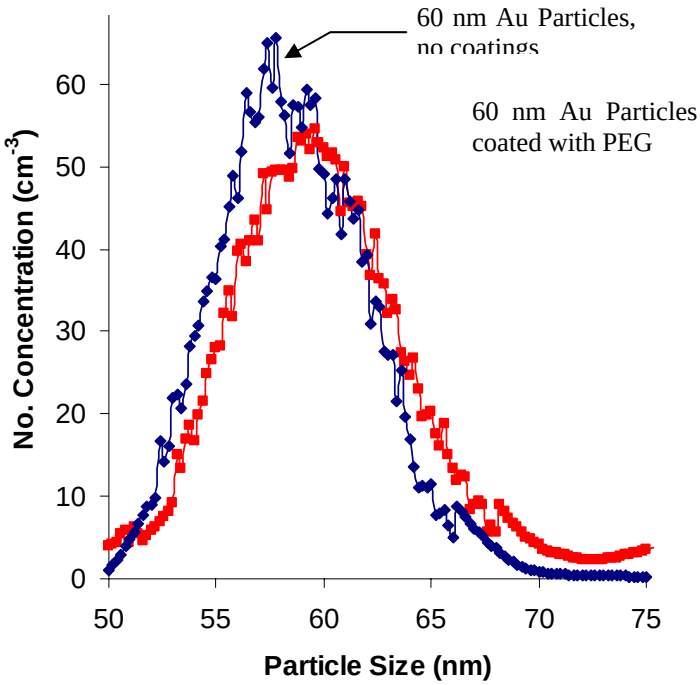
Major accomplishments: Gold nanoparticles of 10 nm and 60 nm sizes have been successfully modified with carboxylic acid (negatively charged), tertiary amine (positively charged), and polyethylene glycol (neutral, hydrophilic, bio-compatible) terminated SAMs as characterized using X-ray photoelectron spectroscopy (XPS). After optimizing the DMA operating conditions so that small size differences in coated particle are observable, a shift in particle size of 0.4 – 1.4 nm after coating with polyethylene glycol was observed for a 60 nm Au colloid. We have also successfully coated 20 nm gold particles with thiolated homo-oligonucleotides of thymine (T_nSH, where n = 10, 20, and 30); DMA results indicate a monotonically increasing trend in the brush length for this series. We expect that an optimized size differentiation of ~ 0.2 nm can be obtained using our DMA methods. Our current work is directed toward increasing the resolution of this analysis tool.

Impact: Gaining proficiency in quantitative and reproducible characterization of organic and biological coated nanoparticles will aid the NCL in their goal of facilitating nanotechnology as a primary driving force for advances in cancer research.

Future plans: Our future goals include modification and characterization of gold nanoparticles with DNA oligomers followed by DMA analysis, including optimization of DMA running conditions for quantitative and reproducible characterization of gold nanoparticles modified with organic and biological coatings.

Figures:





Self-assembly of DNA-Wrapped Carbon Nanotubes for Sensing Applications

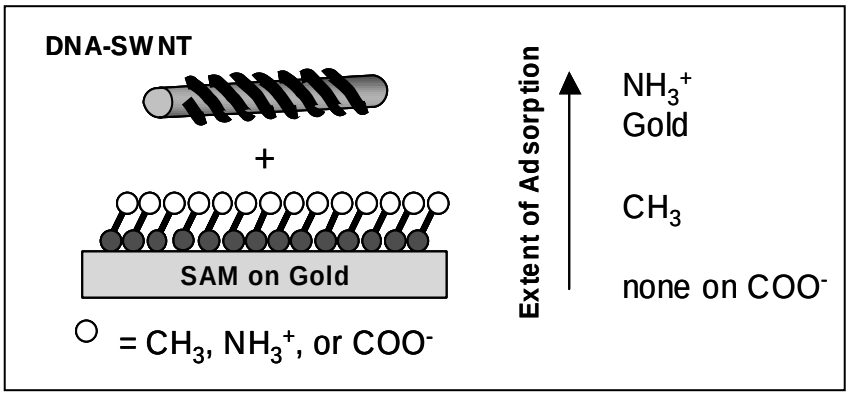
Authors: *R. Zangmeister, J. Maslar, M. Tarlov (836), and G. Gillen (837)*

CSTL Program: Technologies for Future Measurements and Standards

Context: Carbon nanotubes (CNTs) are promising materials for chemical and biological measurement and sensing technology applications. Several studies have shown that the electrical conductivity of CNTs is extremely sensitive to changes in the local chemical environment, a property most likely resulting from the fact that all carbon atoms of CNTs reside at the surface. Some researchers have reported near single molecule detection capabilities with CNT-derived conductivity sensors. In contrast, other groups have reported much more modest sensitivities. These discrepancies along with other irreproducible behaviors that have plagued CNT sensing studies are most likely due to the inherent polydispersity (i.e., metallic and semiconducting) of CNT samples and the difficulty in precisely locating and assembling CNTs in sensing devices. One promising approach to these major challenges is to use single-stranded DNA (ssDNA) to disperse single walled nanotubes (SWNTs) as pioneered by Zheng and coworkers at Dupont. We postulate that the ssDNA moieties will also allow for controlled placement of SWNTs onto nanodevice test structures based on ssDNA-surface interactions.

Approach: Our approach is to study the adsorption of DNA-SWNT hybrid materials on model self-assembled monolayer (SAM) modified surfaces to determine which chemical functional groups can be used to anchor DNA-SWNTs to surfaces. The long-term goal is to use organic monolayers to direct the placement of SWNTs with nanometer resolution to fabricate conductometric-based sensing devices. Reflection absorption FT-IR (RAIRS), micro-Raman spectroscopy, and secondary ion mass spectrometry (SIMS) imaging are used to determine whether DNA-SWNTs can be differentially deposited based on affinity towards chemically patterned surfaces.

Major Accomplishments: We have determined that DNA-SWNT hybrid materials adsorb to model self-assembled monolayer (SAM) surfaces with the affinity order towards terminal chemical functionalities: NH_3^+ > gold >> CH_3 >>> COO^-. The attraction between the DNA/CNT hybrid material and these surfaces was anticipated based on prior knowledge of the interactions of ssDNA on model surfaces. The negative charge associated with the ssDNA causes the DNA/CNT material to adsorb to positively charged amine terminated surfaces due to electrostatic interactions. Similarly, the adsorption of the hybrid material on bare gold surfaces is likely due to the strong chemisorption of DNA bases on gold surfaces. The minimal attraction of the DNA/CNT hybrid material to neutral surfaces is attributable to weaker hydrophobic interactions.



SIMS analysis of patterned SAM surfaces (alternating NH_3^+/CH_3 grid pattern of ca. 10 μm) that were exposed to solutions of DNA-SWNT materials revealed that DNA-SWNTs do not differentially deposit based on the patterned SAM surface. Large bundles of DNA-SWNT

materials were observed on the surface with no commensuration with the underlying chemically patterned surface. This observation suggests that the attraction between DNA-SWNT species may dominate their behavior at the solution surface interface and obstructs patterning of these materials at the micron size scale examine here.

Impact: These studies indicate that organic monolayers can be used to deposit DNA-wrapped SWNTs on surfaces. The ssDNA of the DNA-SWNT hybrid appears to be in a chemical environment similar to that of free DNA such that it can adsorb predictably to model SAM surfaces. The affinity towards specific functional groups is not great enough to differentially pattern DNA-SWNTs on a micron size scale.

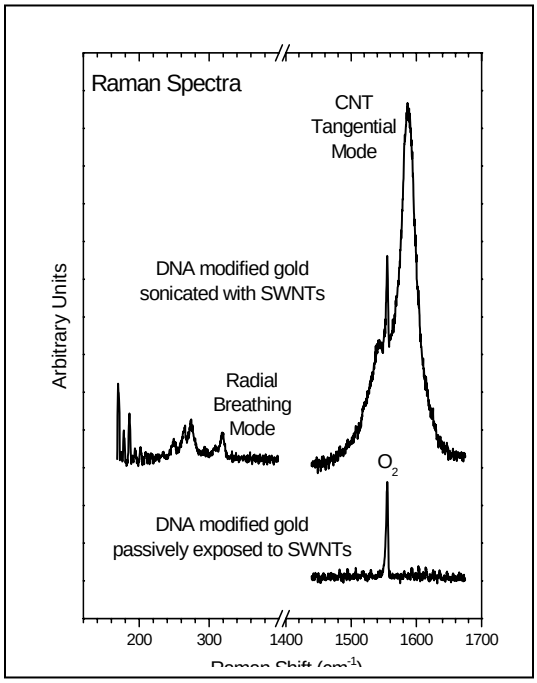
Carbon Nanotube and Thiol Tethered ssDNA Interactions on Gold

Authors: *R. Zangmeister (836.04), J. Maslar (836.07), and J. Kushmerick (837.03)*

CSTL Program: Measurement Science for Future Standards and Technology (CSTL 2006 Exploratory Research Project)

Context: Carbon nanotubes (CNTs) are promising materials for chemical and biological sensing applications. Several studies have shown that the electrical conductivity of CNTs is extremely sensitive to changes in the local chemical environment, a property most likely resulting from the fact that all carbon atoms of CNTs reside at the surface. Some researchers have reported near single-molecule detection capabilities with CNT-derived conductivity sensors. In contrast, other groups have reported much more modest sensitivities. These discrepancies along with other irreproducible behaviors that have plagued CNT sensing studies are may be due to the inherent polydispersity (i.e., metallic and semiconducting) [is multi-wall vs swnt dispersity an issues, seems like it. Does this mean that ssDNA binds preferentially to swnts over multi-wall tubes? If so, then that needs to be made clear.] of CNT samples and to the difficulty in precisely assembling CNTs in sensing devices. One promising approach to these major challenges is to use single-stranded DNA (ssDNA) to disperse single walled nanotubes (SWNTs) as pioneered by Zheng and coworkers at Dupont. The ssDNA wraps around the SWNT and imparts a negative charge on the DNA/SWNT hybrid material that allows for rudimentary purification of metallic vs. semiconducting SWNTs by anion-exchange chromatography. Our approach is to build from this scientific discovery a method of purifying SWNTs using a DNA modified solid support.

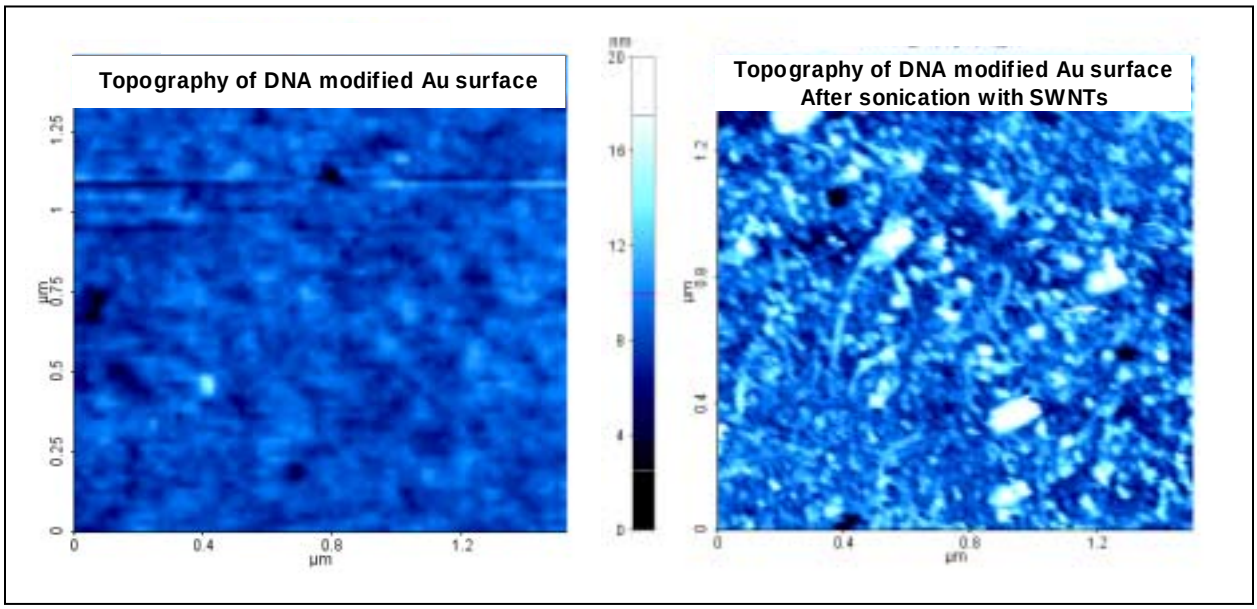
Approach: Our approach is to build from solution based ssDNA-SWNT dispersion technology a method of purifying SWNTs using a DNA modified solid support. We postulate that the DNA on the solid support will wrap around the SWNTs when sonicated in the same manner as free DNA reported previously. The advantage of using DNA that is attached to a solid support is that once the DNA-SWNT hybrids form, we will be able to achieve a primary separation by removing the solid support from the free DNA / SWNT solution. The solid support also serves as a platform for characterization of the DNA-SWNTs upon separation.



Major Accomplishment(s) The adsorption of SWNTs to DNA modified gold surfaces were examined using Raman spectroscopy and atomic force microscopy (AFM) with and without sonication. It was found that the SWNTs do not adsorb to DNA modified gold surfaces without the aid of sonication as evaluated by Raman spectroscopy; CNTs have high Raman cross sections and distinct Raman scattering signatures which enable definitive confirmation of the presence or absence of CNTs on a surface. SWNTs were found to interact with DNA modified gold surfaces with sonication as evidenced by Raman scattering experiments and AFM. Raman spectra confirm the presence of CNTs on the surface with intensities in both the tangential mode (strong) and

radial breathing mode (weaker) regions expected for CNTs. Multiple peaks present in the radial breathing mode region indicate that there is a distribution in diameters of the SWNTs. AFM images before and after sonication indicate that SWNTs are present at the DNA modified gold surface as single nanotubes and in bundles.

Impact: SWNTs were successfully attached to DNA modified gold surfaces through sonication. The selectivity of this process is still under investigation. These findings can also be applied to the directed deposition of SWNTs to DNA modified surfaces.



Future Plans: We plan to explore further the interaction of SWNTs with various DNA compositions, sonication times, and power levels to optimize the specificity of the DNA-SWNT interaction for specific populations (size and electronic character) of nanotubes. Other variables that may be explored will be the length, and the density of the DNA sequences on the solid support surface.

Outputs: These results were received favorably at the AVS 53rd International Symposium [Zangmeister, R. A.; Maslar, J.; Kushmerick, J. " Carbon Nanotube and Thiol Tethered ssDNA Interactions on Gold," *AVS 53rd International Symposium and Exhibition* San Francisco, Nov. 12 - Nov. 17, 2006], and are being prepared for submission to a peer-reviewed journal.

Atomic Layer Deposition – Process Models and Metrologies

***Authors**: J.E. Maslar, W.S. Hurst, and D.R. Burgess, Jr. (838)*

CSTL Programs: Microelectronics

Context/Purpose: Atomic layer deposition is increasingly being utilized to deposit the thin (nanometer-scale), conformal layers that are required for many microelectronics applications, including high κ gate dielectric layers, diffusion barrier layers, and DRAM dielectric layers. However, significant developmental issues remain for many of these applications. The goal of this work is to provide validated, predictive atomic layer deposition (ALD) models and in situ diagnostics for ALD processes.

Introduction: Technology computer-aided design (TCAD) has become a vital design tool for the semiconductor industry. ALD is a relatively new fabrication critical to to the complex manufacture of todays and next generation semiconductor devices. Validated, predictive ALD process models are critical to successful prediction of equipment influences on film properties, thereby providing potential solution to many atomic layer deposition (ALD) process development issues. TCAD has been identified in the 2005 International Technology Roadmap for Semiconductors (ITRS) as "one of the few enabling methodologies that can reduce development cycle times and costs." [2005 ITRS, Modeling and Simulation, page 1] However, many difficult challenges to the development of validated, predictive ALD process models have also been identified, including chemical data (e.g., rate constants, cross sections, surface chemistry); reaction mechanisms, and reduced models for complex chemistry. In addition to a lack of reliable fundamental physical and chemical data, experimental validation has been identified as a "key difficult challenge across all modeling areas." [2005 ITRS, Modeling and Simulation, page 1] Further, with respect to experimental validation, "One of the major efforts required for better model validation is sensor development and metrology, especially for models predicting the fabrication and behavior of ultra-thin films". [2005 ITRS, Modeling and Simulation, page 17] The objective of this project is to assist in solving some ALD developmental issues by providing validated, predictive process models and associated *in situ* metrologies for ALD process diagnostics and control.

Accomplishments: This project involves two primary directions: development of *in situ* metrologies sensitive to ALD chemistry and development of ALD chemical reaction mechanisms. ALD process models are being created by incorporating chemical reaction mechanisms developed at NIST into commercially available computational fluid dynamics (CFD) code that simulates the gas flow and temperature fields in an ALD reactor. Unlike chemical vapor deposition processes which is dominated by gas phase processes and are still widely used for relatively thick film deposition, atomic layer deposition is a surface chemical process that deposits films at or near single molecular thickness. This is accomplished by dosing the deposition surface initially with a monolayer of water molecules followed by the admission of the second reactant to the process chamber and reaction with the water layer to form the desired film.

Experimental validation of overall process models are accomplished by modeling the performance of custom-built, research-grade ALD reactors with optimized optical accessibility and benchmarking the numerical results with experimental data. These data are obtained using various measurement techniques, including vibrational spectroscopies and mass spectrometry. Hafnium oxide (HfO_2) ALD, using tetrakis(ethyl-methylamino) hafnium (TEMAH) and water or

tetrakis(dimethylamino) hafnium (TDMAH) and water, has been selected as the chemical system for primary investigation.

Research-grade, optically-accessible ALD reactors have been designed and constructed with full optical access for surface and gas-phase Raman and FTIR spectroscopic measurements. An associated pulsed gas delivery system has been designed and constructed. HfO_2 films have been deposited with ALD under a variety of process parameters using TEMAH or TDMAH and water. Films have been characterized with a number of techniques, including vacuum ultraviolet spectroscopic ellipsometry (VUV-SE), as illustrated in Fig. 1, X-ray photoelectron spectroscopy, atomic force microscopy, X-ray diffraction, Fourier-Transform infrared (FTIR) spectroscopy, and deep UV Raman spectroscopy. [comments aboaut film quality?]

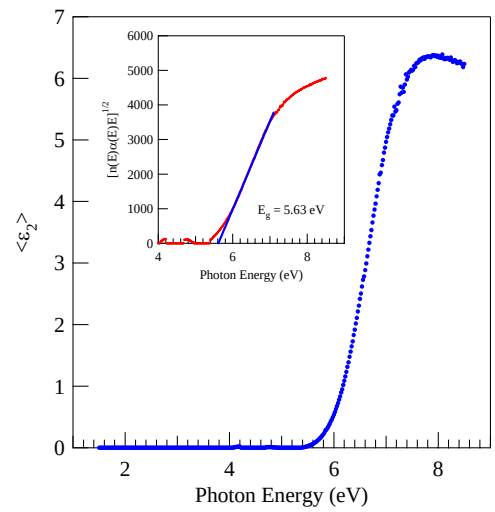


Figure 1. Imaginary part of the complex dielectric function as a function of photon energy for HfO_2 ALD film grown at 200 °C as determined using VUV-SE. The inset illustrates determination of band gap energy by extrapolation of the expression $[n(E)a(E)E]^{1/2}$ to zero (data courtesy of N.V. Nguyen).

In situ gas phase FTIR spectroscopic measurements have been performed during HfO_2 film deposition and have been shown to be sensitive to deposition reactants, TEMAH, and products, N-methyl-ethanamine, as illustrated in Fig. 2. In addition, *in situ* FTIR measurements during TEMAH injection pulses were shown to be sensitive to TEMAH decomposition in the delivery system. Adequate reference spectra could not be located for TEMAH or N-methyl-ethanamine (MEA), a gas phase product of the TEMAH and water ALD reaction. Hence, infrared and Raman vibrational frequencies were calculated with Density Functional Theory using the B3LYP/LANL2DZ method. The calculated frequencies were compared to measured infrared spectra obtained in the ALD reactor and tentatively identified as TEMAH and MEA as shown in Fig. 3.

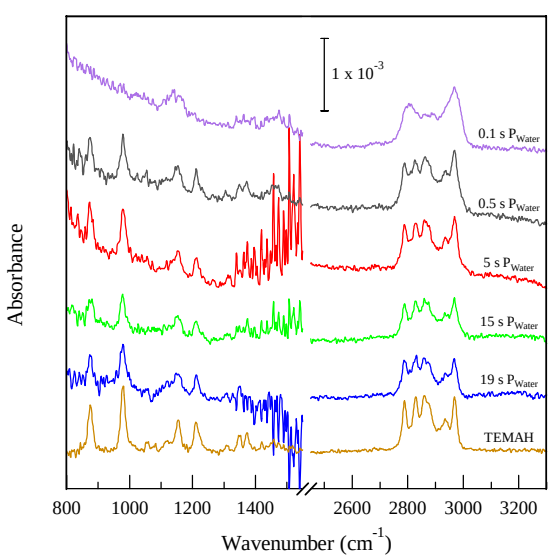


Figure 2. Gas phase FTIR spectra as a function of helium purge time following a water pulse.

Three dimensional CFD models for gas flow and temperature fields have been developed for various reactor geometries, including optically-accessible reactor designs, and used to model flow and temperature under various process conditions, as shown in Fig. 4. In addition, time-resolved precursor distributions have been modeled, as shown in Fig. 5. The results from these models have been used to help optimize reactor designs, especially optical window

design, and deposition conditions. Chemical reaction mechanism models for HfO_2 ALD are being developed for use with these three dimensional flow and temperature models to simulate the entire ALD process.

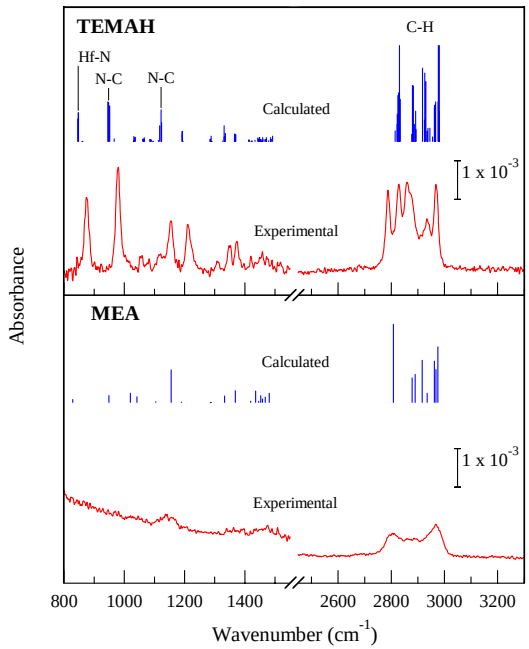


Figure 3. Comparison between calculated and measured spectra of TEMAH and MEA.

Molecular structures and energies for precursors, adsorbates, intermediates, and transition states have been calculated using ab initio and density functional theory quantum calculations for ALD of Al_2O_3 from TMA and water and HfO_2 from TEMAH or TDMAH and water. Although the primary focus of this work is on HfO_2 ALD, Al_2O_3 ALD is also being investigated as a model system for two main reasons. First, there has been significant work on Al_2O_3 ALD, and consequently, there are adequate experimental data for use in chemical mechanism validation. Second, aluminum is more amenable to quantum calculations than hafnium, a transition metal. It is expected that lessons learned in developing an ALD model for Al_2O_3 ALD will be useful in development of an HfO_2 ALD model. For Al_2O_3 ALD, prototypical small cluster ($Al_xO_yH_z$) species have been utilized to represent the surface layer. Rate expressions based on calculated structures and energies have been derived using transition state theory. High level ab initio calculations, up to CCSD(T)/aug-cc-pVnZ (n=2-4) have been done for small species to benchmark heats of formation and bond dissociation energies for AlH_nX species (n = 0-2, X = H, F, Cl, OH, NH_2, CH_3). Additional calculations will be done to provide higher level corrections (*e.g.*, core-valence, relativistic, etc). A Website http://srdata.nist.gov/ckmechx/ (external) and http://h105097.nist.gov/ckmechx (internal) has been made available through the NIST Standard Reference Data website. This site currently contains bibliographic and thermochemical information of silicon hydrides, halocarbons, and organometallic compounds import to semiconductor processes, including information pertaining to ALD and chemical vapor deposition of aluminum, Al_2O_3, and other related ALD systems (*e.g.*, Zr, Hf, etc.), as well as a significant amount of information pertaining to hydrocarbon-based reactions.

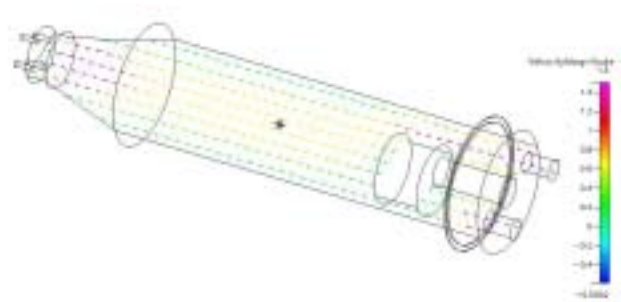


Figure 4. A two dimensional gas velocity profile slice obtained from a full three dimensional reactor model.

Impact: Successful development of validated ALD process models and *in situ* process diagnostics should result in improved efficiency of reactor design and deposition condition selection and optimization, resulting in savings of time and money and increased utilization of ALD.

Future Directions: During the upcoming year, *in situ* gas phase and surface optical measurements will continue in an effort to provide model validation data as well as develop suitable *in situ* diagnostics for ALD processes. Concurrently, we will search for correlations between specific film deposition steps uncovered by the more sophisticated optical methods with signals from conventional process monitors, such infrared absorption spectroscopy and mass spectrometers. In addition, we will attempt to correlate data measured *in situ* at or near the deposition surface with data measured in the exhaust stream in an effort to qualify the results of sensors designed for use on reactor exhaust lines.

Publications:

D.R. Burgess, Jr., J.E. Maslar, W.S. Hurst, E.F. Moore, W.A. Kimes, and N.V. Nguyen, "Atomic Layer Deposition: Process Models and Metrologies," *Characterization and Metrology for ULSI Technology: 2005 International Conference*, edited by D. G. Seiler et al., AIP Conference Proceedings 788, Melville, NY: American Institute of Physics, 2005, pp. 141-146.

J.E. Maslar, W.S. Hurst, D.R. Burgess, Jr., W.A. Kimes, and N.V. Nguyen, "*In Situ* Characterization Of Gas-Phase Species Present During Hafnium Oxide Atomic Layer Deposition," Electrochemical Society Transactions, 2006, in press.

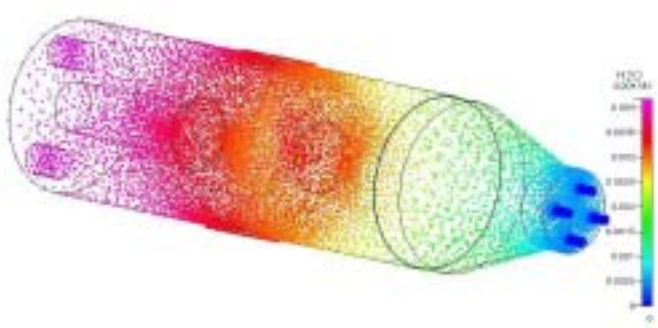


Figure 5. A three dimensional mass fraction profile in an optically-accessible reactor showing the water mass fraction distribution after 3 seconds of helium purge following a 0.1 second long water injection.

Relative Intensity Standards for Raman Spectroscopy

Authors: W.S. Hurst (836) and S.J. Choquette (831)

Program Identification: Industrial and Analytical Instruments and Services

Context: 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 with a limited lifetime, and employs a radiation source that is spatially different from the Raman process. These limitations can be avoided by using luminescent glass artifacts of known relative irradiance. NIST has developed luminescent glasses for intensity calibration for use with popular laser excitation wavelengths that are available as a set of SRMs traceable to NIST primary radiometric standards. The advantage of these glasses is their ease of use, the photostability of the luminescence, and their cost relative to a calibrated white-light irradiance source. 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 is being maintained so that methods, standards, and techniques developed by NIST are widely accepted by the industry.

Introduction: Standard Reference Materials® SRMs 2241 through 2243 are certified spectroscopic standards intended for the correction of the relative intensity of Raman spectra obtained with instruments employing laser excitation wavelengths of 785 nm, 532 nm or 488 nm/514.5 nm. These SRMs each consist of an optical glass that emits a broadband luminescence spectrum when illuminated with the Raman excitation laser. The shape of the luminescence spectrum is described by a polynomial expression that relates the relative spectral intensity to the Raman shift with units in wavenumber (cm^{-1}). This polynomial, together with a measurement of the luminescence spectrum of the standard, can be used to determine the spectral intensity-response correction which is unique to each Raman system. The resulting instrument intensity-response correction may then be used to obtain Raman spectra which are corrected for a number of, but not all, instrument dependent artifacts.

Major Accomplishments: A paper has been written that summarizes the properties of the SRMs and provides a number of experimental details and results that are of importance to the user community that will employ them for the routine calibration of the intensity response of Raman spectrometers. This paper has been accepted for publication and will be a Feature Article, currently planned for the February, 2007 issue of Applied Spectroscopy. In addition to the spectrometer intensity calibration, there is interest in developing a methodology for the validation of the calibration process. This validation can be accomplished by the determination of peak area ratios of intensity corrected spectra obtained from spectral measurements of previously characterized spectra. A current choice is to use the spectrum of cyclohexane, since this chemical is currently an ASTM standard for the measurement of Raman shift, as a check on the spectrometer wavelength calibration. NIST has shown that measurements of the peak area ratios of cyclohexane can exhibit significant systematic variations that are dependent upon the cuvette placement relative to the collection lens focal point of the spectrometer and on the properties of the laser beam. This result has implications for the development of protocols for the validation of the intensity correction procedure and was included in the paper. Work this year was to finish

these measurements to complete a study that covered excitation wavelengths of 488 nm, 514 nm, 532 nm, 647 nm, 752 nm and 785 nm.

In addition, NIST (Choquette, main author) wrote for ASTM Subcommittee E13.08 a Standard Guide for the determination of Raman spectrometer resolution that is currently in the process of being adopted by the Subcommittee.

Impact: This program is providing industry with an inexpensive and easy means for calibration of the Raman spectral intensity. NIST standards will promote the acceptance of Raman spectroscopy as a tool for process control in the chemical and pharmaceutical industries and will provide a means for instrument qualification as required by regulatory agencies such as the FDA. The reviewers expect the paper in Applied Spectroscopy will become the 'definitive paper' on the topic.

Future Plans: A study will be done on the systematic errors that can result from either white light-based or luminescent-based relative intensity calibration of dispersive spectrometers that use two-dimensional CCD detectors (which almost all modern dispersive instruments do). Division 831 (Choquette) is developing a luminescent glass SRM for use at 1064 nm (FT-Raman spectrometers). Collaborative work with ASTM E13.08 will continue.

Output: Paper: "Relative Intensity Correction of Raman Spectrometers: NIST SRMs 2241 through 2243 for 785 nm, 532 nm and 44/514.5 nm Excitation', S.J. Choquette, E.S. Etz, W.S. Hurst, D.H. Blackburn and S.D. Leigh, Appl. Spectrosc. (to be published).

Influencing the "injection barriers" into prototype molecular wires through metal-molecule coupling

Authors: *R. D. Van Zee and C.D Zangmeister (836)*

CSTL Project Area: Technologies for Future Measurements and Standards

Purpose: The drive to introduce organic molecular materials into electronic device applications, (organic electronics) is motivated by a number of potentially attractive features, such as ease of fabrication, ability to fabricate on flexible substrates, and the wide extent to which organic materials can be functionalized via organic synthetic methods. A range of applications is foreseen for organic field effect transistors and light emitting diodes including, for instance, flexible displays and other low cost flexible electronics.

In addition to replacing inorganic semiconductors in more or less conventional device architectures, organic systems are also of interest in the more speculative, and potentially more revolutionary, area of “molecular electronics”. Here, it is envisioned that the nonlinear characteristics of individual molecules, or small ensembles, will provide the required device functionality, allowing low cost chemical synthetic methods to replace, at least partially, multi-billion dollar semiconductor fabrication lines in the production of nanoscale device structures.

In either application format, charge injection at a molecule-contact interface plays a vital role in controlling transport and, thus, potential device performance. Interfacial charge injection is dictated by chemical bonding and the resulting band line-up between the Fermi level of the contact and transport levels of the molecule. Information relating to band line-up is difficult to obtain using conventional techniques in the case of the single-molecule length-scale systems of interest in molecular electronics. We have employed a combination of one-photon (He I resonance excitation) and two-photon photoelectron spectroscopy, using sub-picosecond Ti:sapphire laser-based excitation, to determine the electronic structure, including injection barriers to both occupied and unoccupied levels on a variety of self-assembled monolayers.

Major Accomplishment: The majority of studies of covalently bound monolayers on metallic surfaces involve thiol-coupling (R-SH) chemistry. Self-assembly of monolayers utilizing thiol chemistry is known to form robust, reproducible monolayers on a variety of metallic surfaces. Prototypical thiol-bound molecular systems have been previously studied on poly- and single crystal gold surfaces. To date charge injection barriers of thiol-bound systems on other metals have yet to be determined. This data is fundamental to develop future devices and standards of molecular-based systems. We have undertaken a study of thiol-bound monolayers on a variety of single crystal metallic surfaces (Ag, Cu, Au, Pt). This data allows us to determine two important factors governing behavior in future devices. First, we gain an understanding in how injection barriers vary on a variety of metal surfaces and how the molecular structure effects the alignment of the molecular orbitals with the metal electronic structure. Second, this allows us to develop models and relationships of how the molecular orbiatals of thiol-bound, and other linking chemistries, are aligned to metal surfaces. From these data we can draw important links and analogous behavior between molecular electronics and semiconductors-based devices.

Impact: These results add important insights to the factors that influence band alignment at metal-organic interfaces, a parameter that plays a critical role in potential applications of organic materials in emerging electronic technologies.

Future Plans: We aim to build upon our previous studies of understanding the affect molecular structure and metal have on controlling band line-up in covalently bound molecular systems. Our future work will look into other linking-chemistries on a variety of metal and semiconducting surfaces.

Publications.

Zangmeister, C.D., Robey, S.W., van Zee, R.D., Kushmerick, J.G., Naciri, J., Yao, Y., Tour, J.M., Varughese, B., Xu, B., Reutt-Robey, J.E., *J. Phys. Chem. B.*, **2006**, 110, 17138.

Figure.

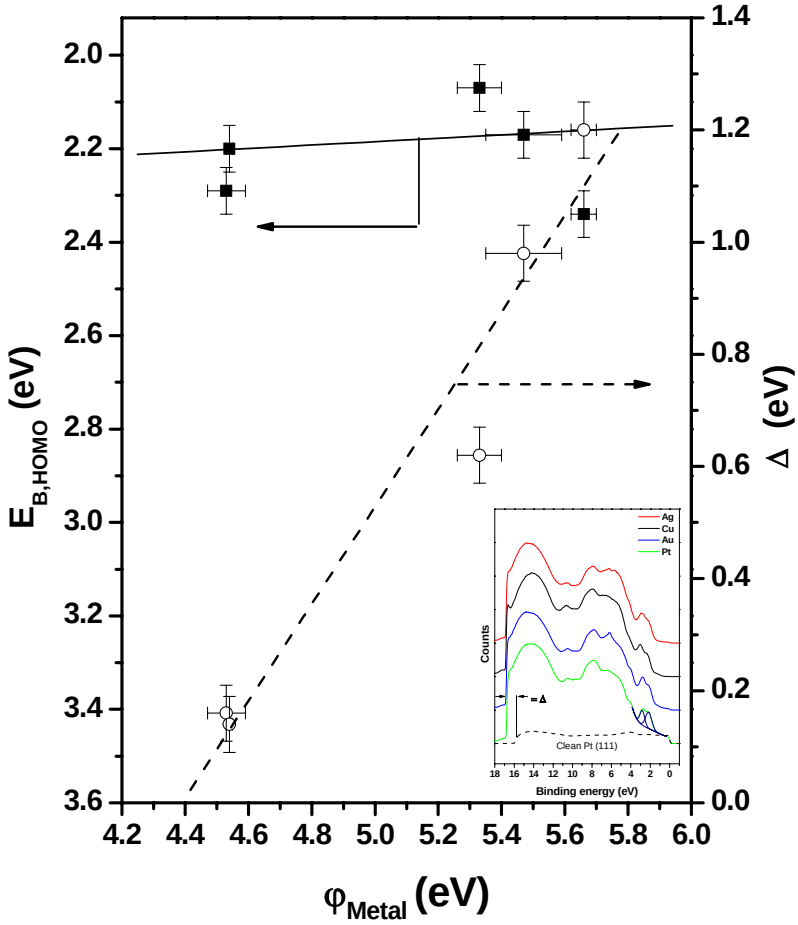


Figure 1. Band alignment parameters of a thiol-bound model molecular wire monolayer on several metal surfaces. One photon photoemission spectra are shown for reference in the inset.

High Performance Metal Oxide Nanostructures for Advanced Solid State Chemical Microsensors

Authors: *K. D. Benkstein, C. S. Mungle, D. C. Meier, S. Garcia and S. Semancik (836), V. Dravid (Northwestern University), V. Golovanov (South-Ukrainian State University) and A. Kolmakov (Southern Illinois University)*

CSTL Program: Industrial and Analytical Instruments and Services

Research underway at NIST, and through collaborations at Northwestern University and South-Ukrainian State University, is aimed at developing nanoparticles, nanofibers, nanowires, nanotubes and related structures of metal oxides for use in microsensor arrays and microanalytical systems to increase sensitivity, selectivity, speed and stability of chemical detection and monitoring. These nanomaterials are being studied as signal transducers for chemical sensors and as elements for upstream filtering and preconcentration of analytes. The approach focuses on using individual structures as well as assembled hierarchical structures for chemical sensing applications where high-performance characteristics (e.g., nmol/mol to pmol/mol sensitivity) are required. These well-defined nanostructures will increase the surface area and active interfacial sites for adsorption and reaction of gas-phase analytes, thereby leading to more sensitive chemical measurements. These structures are also manipulated and aligned so as to study scaling (e.g., differences between a single nanowire and several nanowires in parallel) and nanoparticle-to-nanoparticle interaction effects on chemical sensing phenomena.

The driving force behind much of the nano-materials development in the area of chemical sensors is the significant role that the materials surface plays in chemical detection through interaction with analyte molecules. A prime example of the need for highly sensitive and reliable sensors is in homeland security applications, where the detection of trace levels of highly toxic gases is critical. Specific materials being synthesized and studied include ZnO nanorods, SnO_2, Fe_2O_3 and In_2O_3 sol-gels, and WO_3, Sn and composite Ni-core/TiO_2-shell nanowires. Synthetic methods have been developed based upon the use of chemical additives during nanorod preparation to control the aspect ratios of ZnO nanorods (length:diameter ratios of 5.2 to 0.25, **Figure 1**). The control is effected by additive interaction with specific crystal faces of the ZnO during nanorod growth, either inhibiting or enhancing growth of particular faces to yield different structures. These ZnO nanorods provide a method to study the effect of particular crystal faces upon analyte interaction with the nanomaterials in sensor operation. Sol-gel materials offer a flexible approach to prepare active sensor materials. In collaboration with the South-Ukrainian State University, sol-gel materials (Fe_2O_3, In_2O_3 and SnO_2) have been evaluated as conductometric sensor films. The initial results suggest that these materials may have some value as highly sensitive active elements in a sensor array. Further collaboration with Northwestern University to prepare "nanoline" materials on microhotplate sensor platforms has continued. The nanoline materials offer an alternative method for aligning nanomaterials between electrodes (for other methods being studied, see below), and have the added benefit that they are easily scaled up or down, such that we

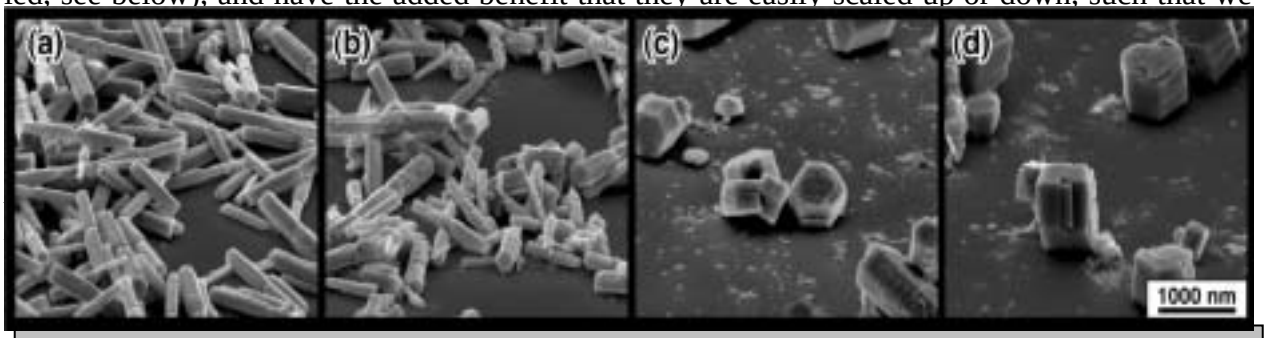


Figure 1. SEM micrographs of crystalline ZnO nanorods showing the effects of growth additives on the aspect ratios: (a) no additive, (b) 10 µM, (c) 20 µM, (d) 40 µM citrate additive.

have been used to control orientation of nanowire deposition for the Ni-core/TiO_2-shell nanowires. Recent work, in collaboration with Southern Illinois University, has demonstrated the viability of single TiO_2 nanowires as conductometric sensors on microhotplate platforms.

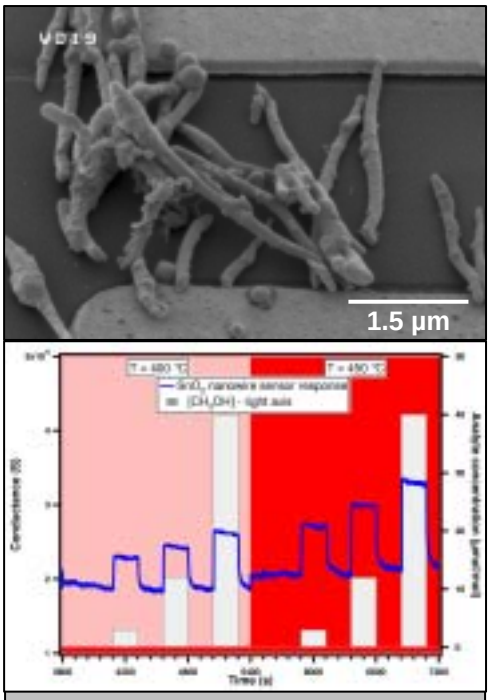


Figure 2. SEM micrograph of SnO_2 nanowires dielectrophoretically positioned between electrodes of a microhotplate sensor (top), and the corresponding conductometric sensor response (bottom).

Higher sensitivity, stability, speed and reproducibility of sensing materials are critical to next-generation sensing devices. These improved performance characteristics, attained by proper assembly of nano-building blocks, are expected to impact many application areas including alarm triggers for counter-terrorism, trace gas detection in space exploration and the monitoring of gaseous biologically-generated compounds for medical diagnostics. Future studies at NIST and at collaborating institutions will elucidate the role of nanostructure and nanomaterials alignment on critical sensor performance parameters, and how further enhancements would be realized through nano-engineering. With the various nanomaterials alignment methods, it will be possible to examine through-wire and across-wire transport, particularly of interest for elucidating the role of grain boundaries (wire-to-wire transport) in chemical sensing. Furthermore, response studies on these aligned nanowires will allow us to perform comparative scaling studies as individual structures are assembled into larger networks and arrays.

Publications:

S. P. Garcia and S. Semancik "Controlling the Morphology of Zinc Oxide Nanorods Crystallized from Aqueous Solutions: The Effect of Crystal Growth Modifiers on Aspect Ratio," *Chem. Mater.*, **2006**, (submitted).

K. D. Benkstein, C. J. Martinez, G. Li, D. C. Meier, C. B. Montgomery, and S. Semancik "Integration of Nanostructured Materials with MEMS Microhotplate Platforms to Enhance Chemical Sensor Performance," *J. Nanoparticle Res.*, **2006**, *8(6)*, 809-822.

K. D. Benkstein and S. Semancik "Mesoporous Nanoparticle TiO_2 Thin Films for Conductometric Gas Sensing on Microhotplate Platforms," *Sens. Actuators B*, **2006**, *113*, 445-453.

Producing and Processing Microsensor Signals to Meet Critical Chemical Monitoring Needs

Authors: *D. C. Meier, B. Raman (Guest Researcher), J. K. Evju, K. D. Benkstein, Z. Boger (Guest Researcher) and S. Semancik (836)*

CSTL Program: Industrial and Analytical Instruments and Services

At the beginning of the 21st century, the United States faces a variety of terrorist threats, is increasingly affected by global warming, has clear needs for efficient alternate energy sources, and demands better and more affordable health care for its aging population. These realities have created an unprecedented need for chemical sensing and monitoring technology that can positively impact the current human condition. These "front-end" chemical analysis needs are being realized at a time when computing and communication advances have produced a highly capable infrastructure for collecting, transferring and utilizing analytical data. Development of low cost chemical monitoring devices for diverse targets in substantially different applications, however, greatly lags behind the computing and communication support tools now available. In addition, due to cost and other logistical factors, existing analytical instruments can be deployed only in an extremely small fraction of the desired settings. In many cases, the analytical demand would best be met with robust, low-power, network-deployable/addressable microsensors.

The detection of relatively low concentrations of a substantial number of different analytes in varied gas phase mixtures represents a broad and challenging problem for sensor researchers. Success in this endeavor, however, could provide critical measurement tools for diverse applications, and important progress has been made toward making tunable, widely deployable microsensors for utility in differing gas mixtures. The NIST array technology combines ~100-µm microhotplate elements with CMOS compatibility, nanostructured sensing films, and artificial neural network (ANN)/statistical signal processing to realize tiny monitoring devices that consume very little power and have been shown to be sensitive at the nmol/mol (ppb) regime and below. In order to recognize target species in variable backgrounds, the signal streams from our conductometric (chemiresistive) microsensors are enriched in two ways – multiple elements with differing sensing films are included in an array format, and each element is individually programmed to cycle through many temperatures as a function of time. The temperature programmed sensing (TPS) operation probes temperature-dependent interactions between the gaseous ambient and sensing materials within the array to produce analytically rich databases that can be analysed to recognize and monitor target molecules. The ultimate capability of these microsensor arrays depends on the selection of sets of transducing materials, the quality and stability of their responses, and the power of the response recognition software.

During the past year, we have made significant advances in developing statistical correlation measures to assess the orthogonality/similarity of responses from sensor materials; this ability greatly assists our selection of film thicknesses and film compositions to incorporate within an array for specific detection application sectors. We have also employed dimensionality reduction techniques, such as linear discriminant analysis (LDA) and principal component analysis (PCA), for visualizing the sensor array response to determine whether sufficient analytical information is available using the chosen materials for species recognition. Figure 1 shows a LDA plot of a 4-element sensor array response to three different toxic industrial chemicals (TICs). It can be clearly seen that the array response to ammonia, hydrogen cyanide and chlorine form clusters that are easily distinguishable from each other and the background. We have also been

able to quantify the variation of signal baselines over extended operating times for our microsensors, and develop data preprocessing routines for drift compensation. Figure 2 demonstrates the effect of our compensation approach, which allows previously trained recognition software to remain viable over months for detection of certain low level toxic industrial chemicals, even as a number of interfering compounds are introduced into the sampled background. These advances are critical to the production of pre-programmed microsensors that can operate in the field for near-real time with multi-species recognition relevant to homeland security, global warming, process control, and other applications.

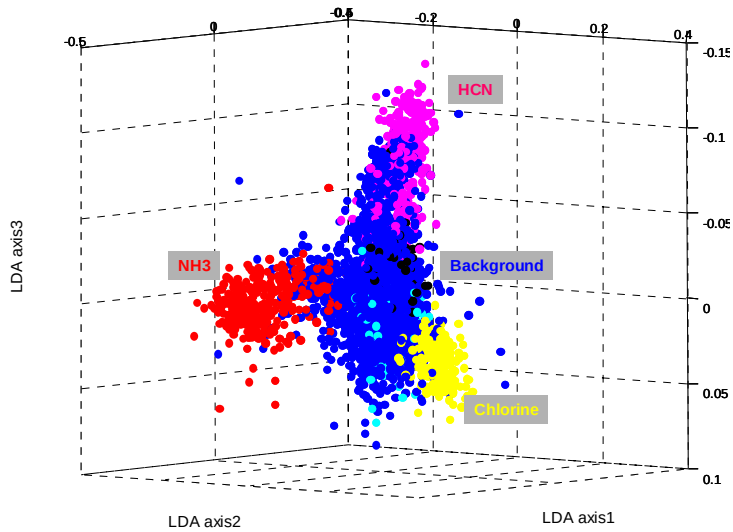


Figure 1: Linear Discriminant Analysis of a four-element array response to different toxic industrial chemicals.

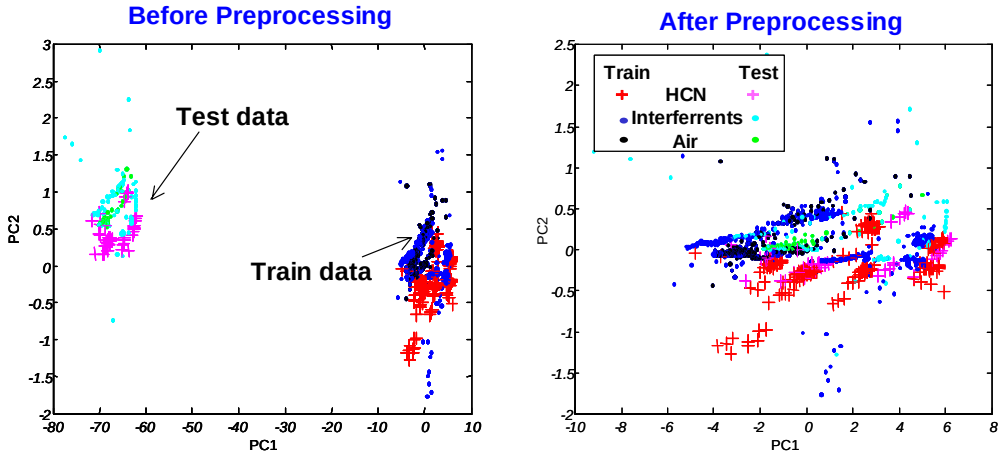


Figure 2: Illustration of the baseline correction technique (note the PC 1 axis scale change) necessary to allow pre-trained recognition software to remain viable for up to two months for detection of TICs.

Gas Standards Based on Optical Spectroscopies

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New applications for gas standards demand high-precision measurements of low concentrations of reactive and nonreactive gases. This challenge requires developing a new generation standards linked to intrinsic molecular properties. We plan to realize and disseminate new primary gas standards using quantitative absorption spectroscopy. To this end, we are combining: (1) frequency-stabilized cavity ring-down spectroscopy (FS-CRDS), (2) low-uncertainty methods of sample preparation and, (3) absolute measurements of absorption line intensities for low-molecular-mass target analytes; e.g., small hydrocarbons, H_2O, O_2 and NH_3. The advantages of CRDS as a primary measurement technique include: compact sample volumes, low uncertainty, high spectral resolution, and high sensitivity.

The goal of this program is to shift the principal realization of traceable gas measurement from consumable artifacts to intrinsic standards. For certain molecules, particularly reactive gases, recent and anticipated advances in spectroscopic measurements will make robust intensity measurements viable for quantitative gas metrology. We anticipate an accuracy rivaling and potentially surpassing traditional measurements using artifact standards.

During 2006 we used frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) to make low-uncertainty measurements of water vapor line intensities for a number of important rovibrational transitions in the near-infrared spectral region. These experiments were built upon our previous high-resolution H_2O line shape measurements which had shown that oversimplified models of line shapes lead to systematic errors in the determination of line intensity and number density. In 2006 we demonstrated that FSCRDS can be used to resolve and deconvolute line blending effects that occur for overlapping and closely spaced transitions. We measured line intensities and relative line positions for blended spectra of H_2O, achieving a relative precision of 0.3% for FS-CRDS measurements of line intensity. We completed an uncertainty analysis indicating a combined relative uncertainty of 0.6% for line intensity determination; a value limited by the accuracy of the transfer standard hygrometer used for water vapor concentration measurements.

An initial study comparing FS-CRDS measurements against NIST CH_4-in-air standard reference materials, ranging from 1 $\mu mol mol^{-1}$ to 100 $\mu mol mol^{-1}$ was also completed. The FS-CRDS measurements probed four closely spaced $2\nu_3$ transitions at approximately 6057.0 cm^{-1}. Current results demonstrate that the long-term precision of the FS-CRDS measurements are comparable to the uncertainties of the gravimetrically prepared standards. It is important to note that the quality of the results is highly dependent upon the data analysis methods. Using a Galatry line shape model, which accounts for both the collisional narrowing and the pressure broadening of the line profile significantly improves the results compared to the results obtained using simpler line shape models. Additionally, this work produced line intensity values linked to NIST primary gravimetric standards, which can be applied in future measurements to value assign an unknown sample.

We also completed an automated and mobile FSCRDS apparatus, which uses fiber-optic coupled distributed-feedback laser technology, with broader application to other NIST projects involving trace water vapor for humidity standards and atomic-layer film deposition processes. We used this system to measure trace water vapor concentration in ultra-dry streams of N_2. Figure 1

shows a survey spectrum obtained with this apparatus corresponding to an H_2O molar fraction of 4.3 nmol mol^{-1}. We linked FSCRDS measurements to thermodynamic-based primary humidity standards maintained at NIST, achieving a detection limit of better than 0.7 nmol mol^{-1}.

Impact: The realization of intrinsic gas standards based on quantitative absorption spectroscopy will extend NIST capabilities in gas standards to lower concentrations, to reactive species that are unsuitable for long-term storage in cylinders, and to trace impurities in bulk process gases. Additional advantages to customers include: lower uncertainties, coverage of new species, potentially lower cost for standard mixtures, more flexibility in terms of dilution gas(es), and the availability of low-uncertainty molecular property data universally applicable to spectroscopic measurements of gas concentration. Customers include current and new consumers of NIST standard gas mixtures, and users of molecular spectroscopy line intensity data.

This work is relevant to emissions of toxic industrial compounds and emissions from ground and air transportation systems, air pollution monitoring (US Environmental Protection Agency), metrology of high-purity gases for semiconductor and photonics manufacturing, terrestrial and extraterrestrial atmospheric science (National Aeronautics and Space Administration), defense (Department of Defense and Department of Energy), health care diagnostics and homeland security (Department of Homeland Security).

Future Plans: During 2007, we will use FS-CRDS to measure infrared spectral line shapes and line intensities of H_2O (1.38 µm band), CH_4 (1.65 µm band) and O_2 (A-band near 0.76 µm). The portable FSCRDS spectrometer will be coupled directly to NIST primary humidity standards and comparisons with commercial CRDS systems will be implemented. Additionally, we are extending these ultra-sensitive cavity-enhanced capabilities to directly address the DoD/DHS calibration and validation needs of deployed and to-be-deployed chemical detectors.

Outputs:

D. Lisak, J.T. Hodges and R. Ciurylo “Comparison of semi-classical line shape models to rovibrational H2O spectra measured by frequency-stabilized cavity ring-down spectroscopy,” Phys. Rev. A., 73, 012507 (2006).

J.T. Hodges and G.E. Scace, “Developing advanced humidity standards to measure trace water vapor in specialty gases,” Micro, **24**, 59 (2006).

J.T. Hodges and D. Lisak, “Frequency-stabilized cavity ring-down spectrometer for high-sensitivity measurements of water vapor concentration,” Applied Physics B, **85**, 375 (2006).

P.M. Chu, J.T. Hodges, G.C. Rhoderick, D. Lisak, J.C. Travis, “Methane-in-Air standards measured using a 1.65 µm frequency-stabilized cavity ring-down spectrometer,” in Chemical and Biological Sensors for Industrial and Environmental Monitoring, Proc. SPIE , Oct. 2006.

P.M. Chu, C.S. Harden, M. Bishop, D.C. Meier, M. Schantz, “Performance validation strategies for chemical agent detectors based on ion mobility spectrometry,” NISTIR 7326, (2006).

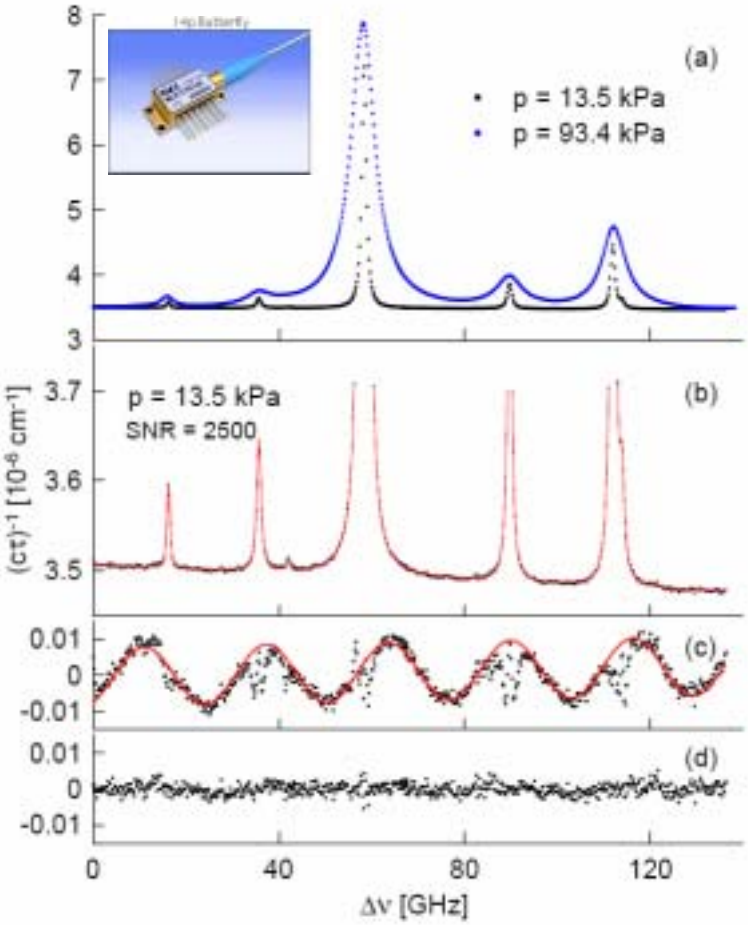


Fig. 1. FS-CRDS absorption spectrum of H_2O absorption near λ = 1.39 μm. (a) measurements. (b) expanded view with Galatry line shape fits to measurements. (c) residual etaloning structure (symbols) and sinusoidal fit (line). (d) fit residuals after removing etaloning structure. The fiber-coupled DFB probe laser is shown in the inset.

Non-Contact Free Carrier Density Measurements for Compound Semiconductors

Authors: *J. E. Maslar and W. S. Hurst (836).*

CSTL Program: Microelectronics

Purpose: Develop non-contact measurement methods for carrier concentration and mobility in optoelectronic materials.

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

Accomplishments: Materials with a range of properties suitable for use in a variety of optoelectronic devices operating at different regions of the electromagnetic spectrum are being investigated. The primary focus is on narrow band gap group III-antimonide materials and wide band gap group III-nitride materials. Spectroscopic systems were optimized for each material system after examining selected thin films of narrow band gap GaSb, GaAsSb, GaInSb, and GaInAsSb and wide band gap GaN, and AlGaN, obtained from various collaborators. Systematic Raman spectroscopic measurements have been performed on epitaxial layers of GaSb, GaInAsSb, GaAs, InP, and GaN with various doping levels and types. An example of a series of Raman spectra is shown in Figure 1.

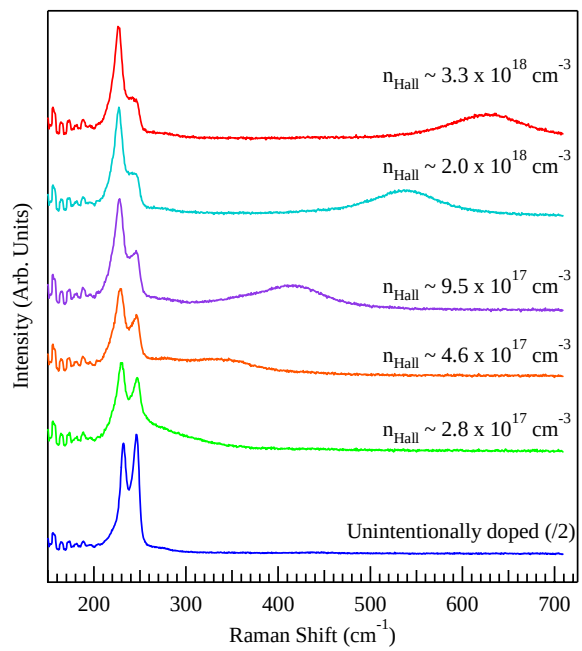


Figure 1. The Raman spectra of n-type doped GaInAsSb epilayers show a strong dependence on carrier density. The carrier density determined from the Hall

Spectral models of various levels of sophistication have been developed for n-type doped GaSb, p-type GaSb, n-type GaInAsSb, p-type GaInAsSb, and n-type GaN. Modeling of the Raman spectra from the different materials requires different spectral models that account for the differences in physical properties that make these materials suitable for different applications. In depth comparisons of the carrier concentrations determined from spectral models to the carrier concentrations determined from

Hall effect measurements have been performed for n-type doped GaSb, p-type GaSb and n-type GaInAsSb. A representative result is shown in Figure 2.

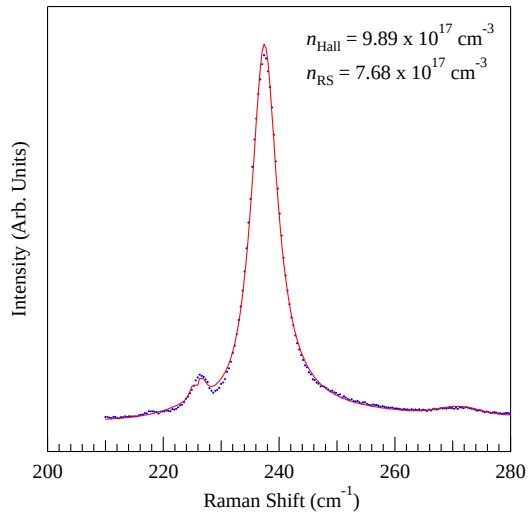


Figure 2. The measured Raman spectrum (dots) and associated best-fit simulated spectrum (solid line) for a p-type GaSb epilayer. The spectral fit corresponds to a carrier concentration of 7.68 x 10^{17} cm^{-3}. A carrier concentration of 9.89 x 10^{17} cm^{-3} is derived from Hall effect measurements.

Impact: The results of this investigation should facilitate the utilization of Raman spectroscopy for spatially resolved, off-line characterization as well as process monitoring and control during film growth and subsequent patterning processes.

Future Directions: In depth comparisons of the carrier concentrations determined from spectral models to the carrier concentrations determined from Hall effect measurements will be performed for p-type GaInAsSb and n-type GaN. In addition, this technique will be evaluated for use on doped GaN nanowires.

Publications:

J.E. Maslar, W.S. Hurst, and C.A. Wang, "*Raman Spectroscopy of n-Type and p-Type GaSb with Multiple Excitation Wavelengths*," Applied Spectroscopy, submitted.

J.E. Maslar, W.S. Hurst, and C.A. Wang, "*Raman Spectroscopic Determination of Hole Concentration in p-Type GaSb*," Journal of Applied Physics, submitted.

Atomic Standard of Pressure

Authors: M.R. Moldover, J.W. Schmidt (836), R.M. Gavioso (Guest Researcher-Istituto Elettrotecnico Nazionale Galileo Ferraris, Torino, Italy), E.F. May (Guest Researcher – Univ. of New South Wales, Australia)

CSTL Program: Industrial and Analytical Instruments and Services

Vision: Develop an accurate primary standard for pressure in the range 0.3 MPa to 7 MPa based on fundamental physical properties of helium.

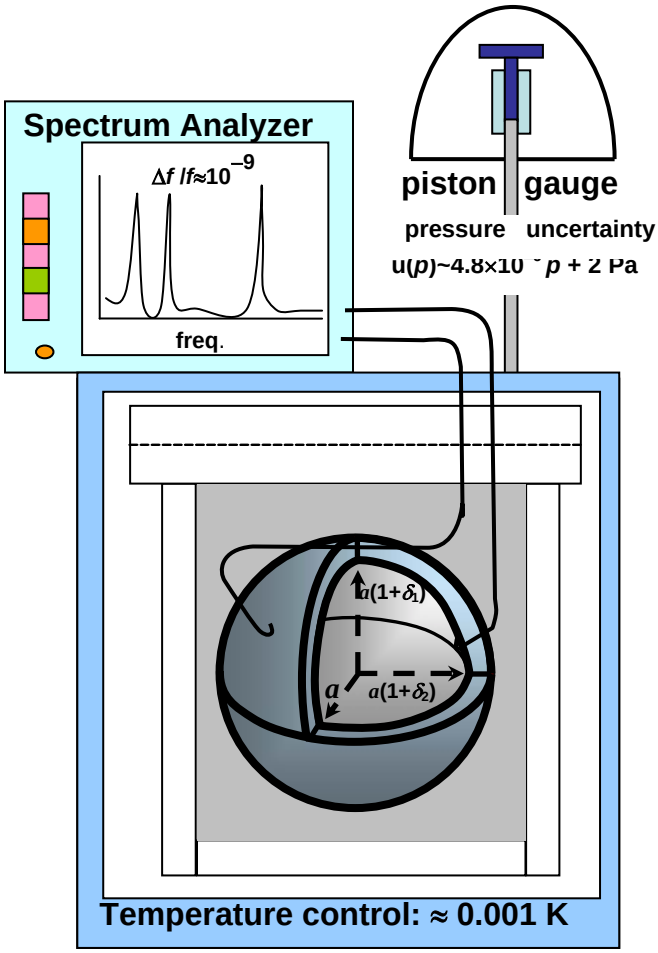
Approach: NIST will determine the pressure $p(\varepsilon,T)$ of helium gas by measuring and calculating the dielectric constant, $\varepsilon(p,T)$. Ultimately, the uncertainties from the theory, impurities, and the electrical and temperature measurements are expected to be smaller than those of existing pressure standards (piston gages). When this occurs, the dielectric constant of helium will become the basis for a new pressure standard. The standard will be disseminated by calibrating piston-cylinder sets and by using the helium standard to measure $\varepsilon(p,T)$ of argon. Argon is chosen because it is readily available in high purity and because its dielectric polarizability is eight times larger than that of helium.

Context: Below 300 kPa, the primary pressure standard at NIST is a 3-meter mercury manometer. Above 300 kPa, the pressure standards are commercially manufactured piston-cylinder sets. These sets are complicated artifacts. In operation, the cylinder and piston deform significantly and the piston rotates continuously to insure gas lubrication. Because of these complications, piston-cylinder sets are calibrated using the primary-standard mercury manometer below 300 kPa and their performance is extrapolated to higher pressures using numerical models of the coupled gas flow and elastic distortions. The extrapolation cannot be checked with existing technologies; thus, it is not fully trusted. Furthermore, piston-cylinder sets exhibit poorly understood specie and gas flow dependencies. When $\varepsilon(p,T)$ of helium becomes the pressure standard, it will be possible to test models of piston-cylinder sets and to reduce the uncertainty in the assignment of their effective area.

Progress: Figure 1 sketches the apparatus that we use to measure $\varepsilon(p,T)$, the dielectric permittivities of helium and argon, in the ranges 0.1 to 7 MPa and 0 to 50°C. We determine $\varepsilon(p,T)$ from measurements of the temperature, pressure, and microwave resonance frequencies of a gas-filled quasi-spherical cavity. The cavity's shape differs from that of a perfect sphere by only a few parts in one thousand. This small distortion is just enough to lift the triple degeneracy of the selected microwave resonance frequencies, thereby facilitating frequency measurements with part-per-billion uncertainties. Figure 2 shows the measurements of $\varepsilon(p,21\ °C)$ and $\varepsilon(p,0\ °C)$ of helium and the deviations of the measured values from the theoretical values. The values measured as the pressure increased and as the pressure decreased for four microwave triplets spanning the frequency range 2.7 GHz to 7.6 GHz are mutually consistent, within the thicknesses of the lines on Fig. 2.

The helium-filled microwave cavity is bounded by walls made of copper-plated maraging steel. The theory must account for the shrinkage of these walls (and the cavity) under applied pressure. We calculated the shrinkage from the isothermal compressibility κ_T of maraging steel samples cut from the same billet as the walls. We determined κ_T of maraging steel with an uncertainty of 0.1 % by measuring the frequencies of the mechanical resonances of the cylindrical samples. This is an advance in the state-of-the art of resonance ultrasonic spectroscopy. During the next

few months, we will reduce the uncertainties of the pressure and temperature measurements. Our colleagues are also reducing the uncertainty of the theoretical calculations of $\varepsilon(p,T)$. Thus, we expect the uncertainty of the new standard to be reduced.



Impacts: (1) This program will revolutionize the realization of pressure standards. (2) In earlier work, we invented the gas-filled, quasi-spherical cavities to simplify acoustic thermometry. Now, NIST and other NMIs are these cavities to determine the imperfections of the internationally accepted temperature scale, ITS–90.

Figure 1. The dielectric permittivity of helium or argon is measured using an quasi-spherical cavity resonator. Each of the selected electromagnetic modes (TM_{11}, TE_{11}, TM_{12}, TE_{12}) are split into 3 sharp resonances. The ratio of the resonance frequency divided by the vacuum frequency of the modes is used to measure the dielectric permittivity of the gas inside the resonator.

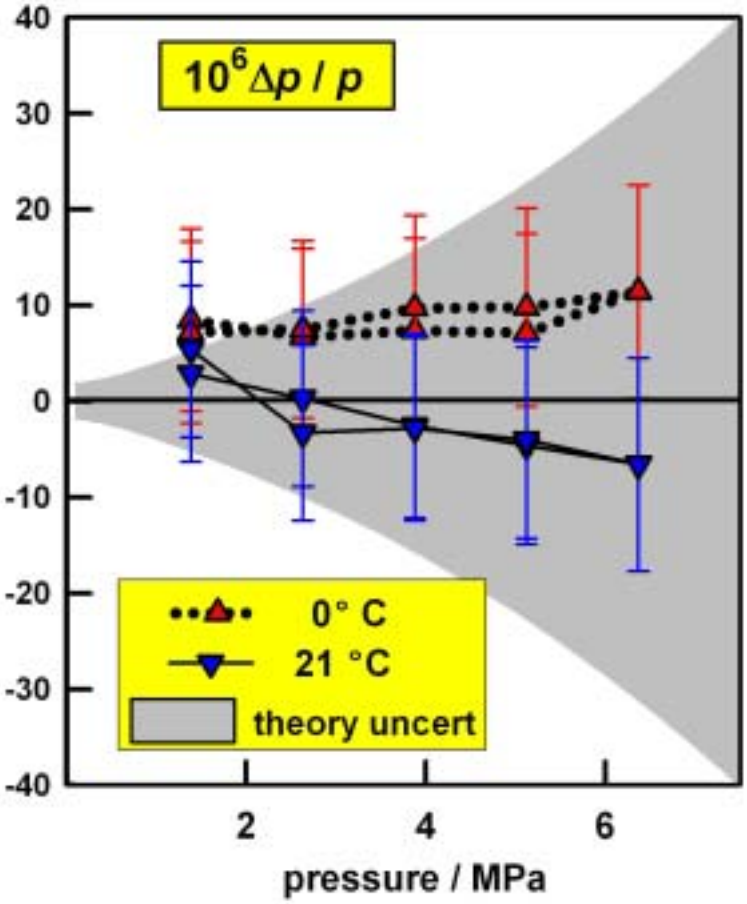


Figure 2. Fractional difference between the pressure determined from the microwave resonance frequencies of a helium-filled cavity and the pressure determined by NIST's standards. The cavity was operated at 0 °C and 21 °C. During the next few months, we expect that the theoretical and experimental uncertainties will be reduced by a factor of two.

Pipeline-Scale Flow Measurement Standards for Natural Gas

Author: *A. N. Johnson*

CSTL Program: Energy and Environmental Technologies

Vision: Provide NIST traceability for custody transfer of natural gas in large pipelines with uncertainties of 0.2 %, or less.

Purposes: (1) Reduce the costs associated with measurement uncertainties for international custody transfer of natural gas and (2) facilitate the sale of US-manufactured flow meters abroad by providing NIST calibrations or NIST-traceable calibrations of such meters.

Context: In 2004, the US consumed 630×10^9 cubic meters of natural gas. Of this total, approximately 16% was imported from Canada through pipelines at a cost of $21 billion. The volume of imported natural gas will continue to increase for the foreseeable future because the US is the largest energy consumer; however, the US holds only 3% of the world's natural gas reserves. (Reference: Energy Information Administration, www.eia.doe.gov.) At present, custody transfer of natural gas in pipelines relies on flow meters (*e.g.*, turbine meters, ultrasonic meters) with calibrations that are NOT traceable to SI units through NIST. The uncertainty of flow measurements provided by private flow laboratories is as large as 0.5 %. NIST, in collaboration with U.S. private flow laboratories, will reduce flow uncertainties to 0.2 % and will establish traceability for flows ranging from 0.7 m^3/s to 10.7 m^3/s.

Traceability between NIST and private flow laboratories is being established with four critical flow venturis (CFVs) calibrated at NIST. Often, CFVs are used as transfer standards to compare the primary flow standards of Natural Metrology Institutes (NMIs) because CFVs are rugged and they have a well understood physics and excellent long term reproducibility. NIST has designed a sequence of measurements starting with CFVs calibrated at NIST in low pressure air and extending to high pressure natural gas with only small increases in uncertainty. Ultimately, the NIST calibrated CFVs will be used to calibrate other the flow standards (*e.g.*, turbine meters) located in private flow laboratories equipped for large flows of natural gas. Upon request, NIST will supervise calibrations at suitable laboratories, thereby providing NIST calibrations of flow meters at lower uncertainties than those available today.

Accomplishments: Thus far, the NIST-calibrated CFVs have been calibrated at two other NMIs. All three NMIs were mutually consistent within 0.05 %. NIST calibrations spaced two years apart demonstrate that the irreproducibility of these CFVs is less than 0.03 %. Having thoroughly characterized these CFVs, NIST has begun to calibrate secondary standards at one of the two privately owned flow laboratories in the U.S. equipped to measure pipeline scale natural gas flows. The NIST calibrated CFVs were arranged in a common plenum and used to calibrate several additional CFV flow meters at higher flows, which in turn were used to calibrate an array of turbine meter reference standards. The privately owned flow laboratory uses these reference standards to calibrate more than 70 % of the flow meters used for the custody transfer of natural gas in the U.S.

Impact: By next year, NIST will offer pipeline scale natural gas flow measurements to U.S. industry.

Future Work: In the coming year we will assess possible flow interference effects resulting from using multiple CFVs in a common plenum, check the consistency of the new turbine meter

calibrations by systematically comparing these reference standards to each other, and publish an uncertainty analysis of the measurement results. Then, NIST will be ready to initiate a key comparison with the other NMIs capable of measuring pipeline scale natural gas flows.

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2. A. N. Johnson and T. Kegel, "Uncertainty and Traceability afor the CEESI Iowa Natural Gas Facility," Journal of Research of the National Institute of Standards and Technology, 109, 345-369 (2004).
3. 3 B. Mickan, et. al., "Comparisons by PTB, NIST, AND LNE-LADG in air and Natural Gas with Critical Venturi Nozzles Agree within 0.05 %", International Symposium of Fluid Flow Measurement (ISFFM) 2006 Conference.