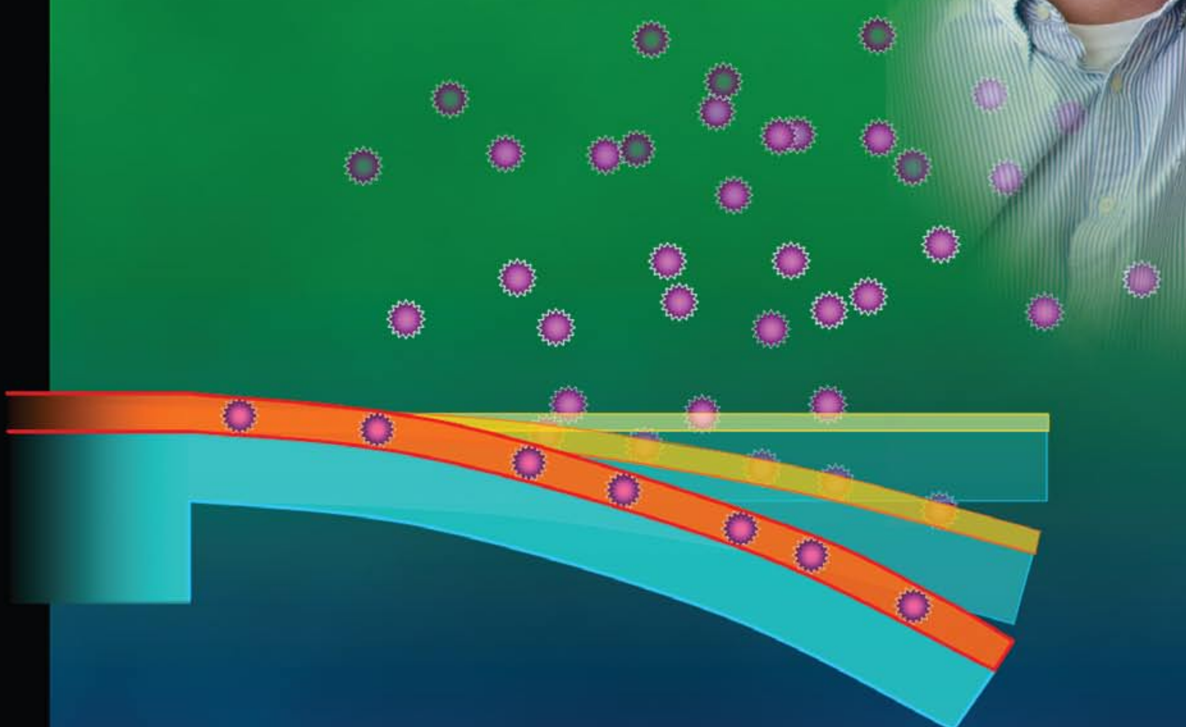
Sniffing the Air

A new Livermore sensor uses minuscule cantilevers to detect dangerous airborne chemicals.



The Livermore sensor research was led by (from left) chemist Brad Hart, former Laboratory chemist Timothy Ratto, and physicist Albert Loui. The artist's rendering represents a side view of a polymer-coated microcantilever responding to the presence of chemical vapors of interest. The chemical molecules (pink balls) are absorbed by the microcantilever's thin polymer coating. When this coating swells, a surface stress is applied to the cantilever, causing it to bend. The more the microcantilever bends, the more its electrical resistance changes.

with an Electronic Nose

THE human nose is a marvel at detecting more than 10,000 different airborne chemicals. For more than a decade, scientists have been attempting to emulate and even surpass the capabilities of the human nose with devices sometimes called "electronic noses." New sensor technologies have been invented to aid medical diagnosis, ensure quality control in the food and beverage industries, detect high explosives in airports, and search for toxic gases in factories.

For more than two decades, Lawrence Livermore scientists have been among the leaders in developing miniaturized electronic tools to detect chemical, seismic, magnetic, pressure, acoustic, and nuclear signals. For example, Livermore researchers have built highly accurate and extremely sensitive sensors that can detect trace amounts of airborne radioactive contaminants emanating from a suspected nuclear weapons facility.

The Laboratory is now working to meet the requests of Departments of Defense and Homeland Security planners for lightweight, accurate, and inexpensive handheld sensors to sniff out deadly chemicals, including chemical weapons on the battlefield and toxic compounds that could be used in a terrorist attack. The ambitious goal is to simultaneously fulfill the requirements of small size, low power consumption, rapid and reliable detection of chemicals at extremely low concentrations, ruggedness for potentially harsh environments, and low cost per unit for mass production and widespread use.

A team of physicists, chemists, and engineers is working toward this goal with a new sensing device that selectively identifies chemicals of interest from a typical background "soup" of airborne compounds, using minuscule diving boards called microcantilevers. The Livermore electronic nose can detect nearly any chemical vapor, including chemical warfare agents, once the sensor has been "trained" to recognize them. The device has reliably detected 11 different chemical vapors, plus the chemical warfare agents VX and sulfur mustard, representing a wide breadth of chemical classes.

Building an Early Warning System

"We want to provide national emergency responders and soldiers in the field with an electronic early warning system for detecting chemical agents, one that will be far more efficient and cost-effective than those currently available," says chemist Brad Hart. "Many sensors can readily detect chemical agents in the low parts per million concentration range with rapid response rates, but those devices are bulky, heavy, require power-hungry electronics, suffer from false-positive readings, and have price tags exceeding $10,000 per unit. We don't believe any commercial sensor system matches the small size, low power consumption, robustness, sensitivity, and other characteristics of our design." Hart leads the team of researchers whose pioneering sensor design was spotlighted on the May 2008 cover of the scientific journal *The Analyst*.

In studying different sensor designs and materials, the team focused on the potential of microcantilevers as transducers to communicate the presence of chemical vapors of interest. The Livermore design is based on the differential bending of a microcantilever made from silicon and wrapped in silicon nitride—a durable, chemically inert material. A final plastic coating that is relatively impervious to water vapor is then applied. The greater the amount of material absorbed by the microcantilever, the more it bends, until a maximum deflection of about 1 percent is achieved. "Microcantilevers have no intrinsic capability to sense chemicals," says physicist Albert Loui. "The application of a swellable coating gives them this capability."

The device is an example of a microelectromechanical systems– (MEMS-) based chemical sensor, which requires specific materials to imbue it with chemical sensitivity. These materials, usually specialized polymer (plastic) coatings, have an affinity for the chemical vapors of interest and undergo a change when interacting with them. In the Livermore design, gas absorption creates volumetric strain; thus, a chemical signal is rendered into a mechanical one.

The sensor technology takes advantage of a physics principle called piezoresistance, which is a change in the electrical conductivity (or resistivity) of a solid material as it is deformed. Piezoresistive microcantilevers are commercially manufactured by standard microfabrication techniques. In the current Livermore prototype, different plastic formulations are applied to each microcantilever, with uncoated microcantilevers acting as electrical references. (See the box at left.)

When a cantilever bends from the swelled coating, its resistance changes, which is measured by an electrical circuit. "We're not measuring mass, as with a mass spectrometer, but rather the electrical resistance," Hart notes. He also points out that a mass spectrometer gives a readout of everything in the atmosphere, but the Livermore sensor is designed for applications in which only one or two specific chemicals are detected.

The current research effort is funded by the Department of Defense's National Consortium for Measurement and Signatures Intelligence Research. Hart works in Livermore's Forensic Science Center, one of only two U.S. laboratories certified as an analytical laboratory for the Organisation for the Prohibition of Chemical Weapons. Much of the sensor research has been carried out at the Laboratory by Hart, Loui, and chemist

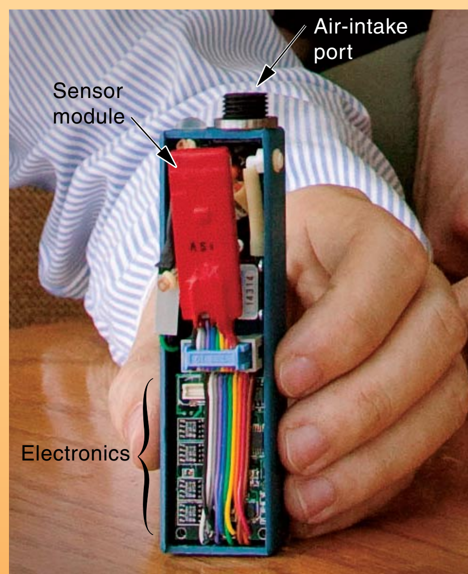
Livermore Sensing Microcantilevers in Action

Laboratory scientists have designed a new chemical detector that uses a pair of commercially manufactured sensor arrays packaged inside a flow cell, exposing both arrays to a common air stream. Each array integrates four rectangular piezoresistive microcantilevers. Six of these microcantilevers (three per side) are coated with six different polymer (plastic) formulations. When gas-phase molecules land on the cantilevers, they diffuse into the polymer, changing its physical and chemical properties.

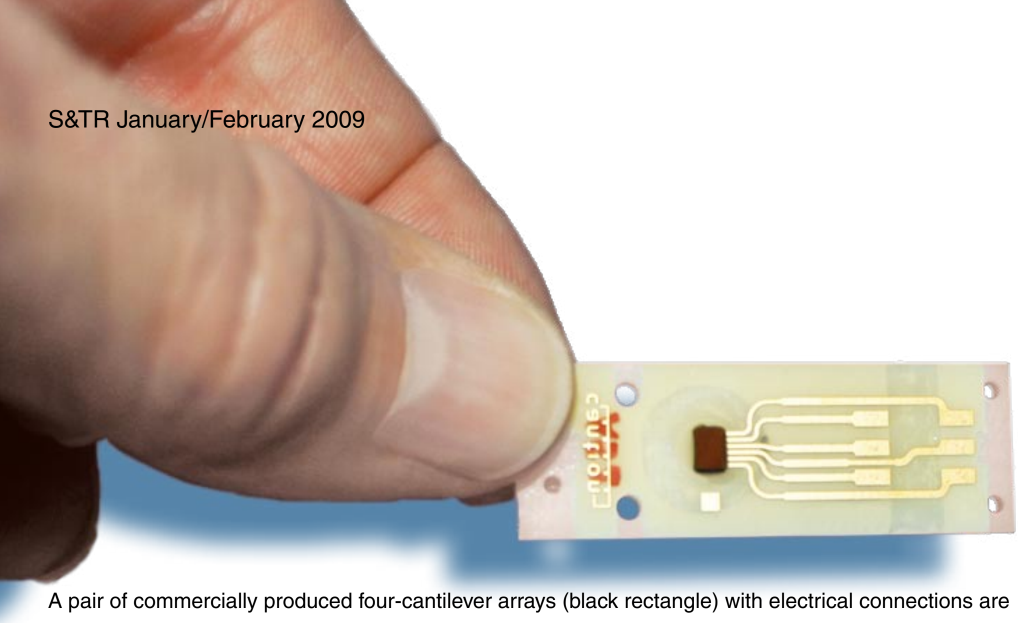
The polymer coating swells as its constituent molecular strands move past one another, changing the coating's physical dimensions and exerting a stress on the underlying silicon substrate. The resulting deflection changes the microcantilevers' electrical piezoresistance, which is readily measured. The amount of swelling is proportional to the amount of material absorbed, and the pattern of swelling among the six microcantilevers indicates which chemical vapor is present.

During operation, each of the six sensor channels continuously outputs a voltage that is proportional to the changes in the piezoresistance caused by the bending of the polymer-coated microcantilevers. These signals, along with the voltages from the two uncoated reference cantilevers, are sent to an electronics module. For each microcantilever, the deflection response is measured with respect to a single reference cantilever. This strategy permits rejection of electronic noise. The reference signal is subtracted from the signal of each cantilever, and the resulting deflection voltages are sent to a laptop computer for processing. On average, it takes 1 to 2 minutes for the software to identify the vaporous chemical.

Once the ambient vapor dissipates, the absorbed molecules will naturally diffuse, and the polymer coatings will dry out, much like wetted sponges. This process can be hastened with added air flow or gentle heating.



During operation, eight microcantilevers inside the sensor module are exposed to chemical vapors drawn in at the air-intake port by a miniature pump. The resulting bending response of the microcantilevers is detected and processed by the device's electronics.



A pair of commercially produced four-cantilever arrays (black rectangle) with electrical connections are combined with Livermore-developed components to create the sensor airflow cell shown here.

Timothy Ratto (formerly of Livermore). Other researchers from Livermore include Tom Wilson, Scott McCall, Erik Mukerjee, Adam Love, Jim Zumstein, and John Chang. Researchers at Oak Ridge National Laboratory, University of Illinois, and Texas Tech University have also contributed to the sensor development effort.

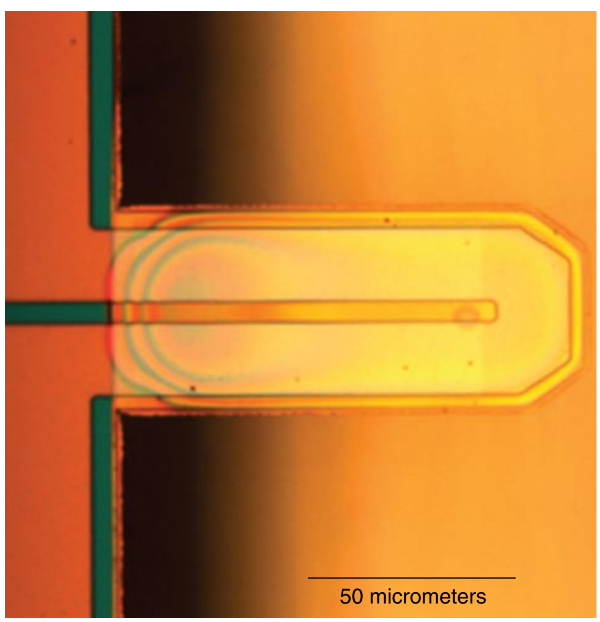
Sensor Requires No Consumables

The prototype sensor system consists of a pair of arrays, each with four silicon microcantilevers. Each cantilever measures 120 micrometers long by 50 micrometers wide by 0.5 micrometers thick. The arrays require no consumable materials (unlike many commercial detectors) and are resistant to common mechanical vibrations. Also, they are commercially available and relatively inexpensive, making the sensor system potentially cost-effective for widespread production and use.

Engineers Zumstein and Chang helped develop the sensor's electronic circuitry, which is based on novel embedded microprocessors. These microprocessors facilitate scalable, multichannel, low-noise, high-fidelity signal processing. The Livermore-designed circuits reduce the electronic noise to levels comparable to those attained with much larger and expensive benchtop systems. The result is greater differentiation of a wider variety of low-concentration chemicals. The sensor system operates on 9-volt, AA, or AAA batteries, using just 750 milliwatts of power, less than a typical cell phone.

Initially, the team found that despite the promise of microcantilevers, some of the materials used in early designs were vulnerable to not only humidity but also high temperatures and corrosive environments. Because of these vulnerabilities, the team chose to coat the microcantilevers with amorphous polyolefins, a common class of plastics. The stiffness of the coatings allows for greater stresses to be exerted on the microcantilevers during absorption of a chemical. The plastic coatings also make them more resistant to corrosive and moist environments. Millions of compositions of polyolefins are available, enabling a different coating formulation to be applied to each sensing microcantilever. Because the thickness of the plastic coating must be precise for the sensor to work, the team developed a method for applying a highly uniform film as thin as a few tens of nanometers. "We have a rich palette of chemical properties to play with when selecting interactions for the volatile chemicals of interest," says Hart.

The set of six deflection voltages collectively represents a signature that uniquely identifies one vaporous chemical. However, the team must first perform calibrations, during which a sensor array is "trained" to identify certain chemical signatures; that is, it must associate the pattern of deflection across the microcantilevers with the presence of a certain volatile chemical.



This photomicrograph shows a rectangular-shaped cantilever (extending to the right) coated with a thin film of vapor-sensitive polymer.

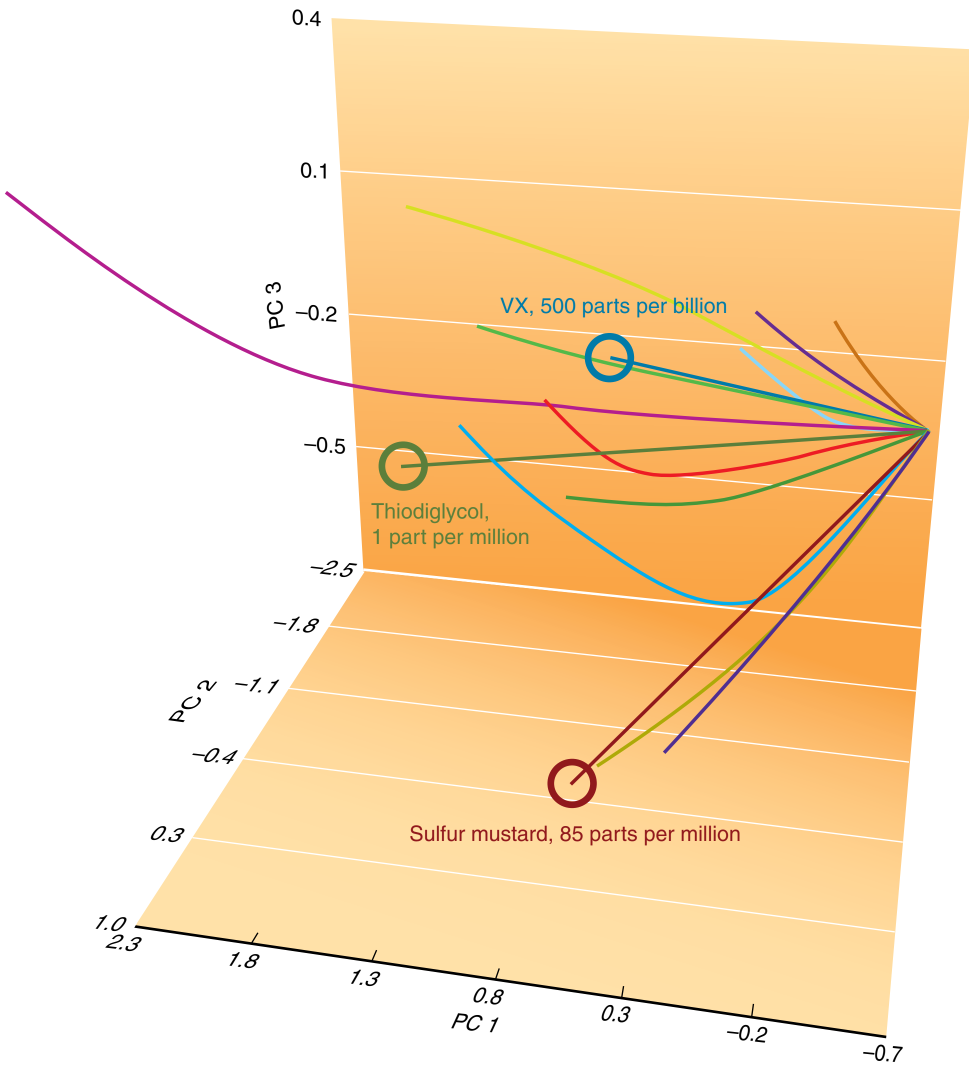
Testing the Unit

In 2008, the prototype sensor was trained to recognize a small library of preexisting chemical signatures based on the collective response of the microcantilevers. Tests were then conducted to gauge performance, in particular with respect to the reproducibility of response and the sensor's ability to discriminate one chemical signature from another as well as from system electronic noise. The microcantilevers were exposed to the chemicals at concentrations corresponding with those to which they were trained, between about 200 parts per million (ppm) and 16 parts per thousand. Prepared vapors were pumped through the sensor at a rate of 10 to 220 cubic centimeters per minute until all six cantilevers achieved maximum deflection. The onset of bending was nearly instantaneous for all microcantilevers following initial exposure to each chemical.

The sensor reliably detected 11 vapors, including hexane, 1,4-dioxane, benzene, toluene, ethyl acetate, acetone, acetonitrile, methylene, chloride, methanol, and isopropanol. The chemical species were selected as simple representatives of several classes: alkane, ether, aromatic, ester, ketone, nitrile, haloalkane, and alcohol.

The sensor also detected the chemical warfare agents VX and sulfur mustard, both of which were synthesized in trace quantities at Livermore's Forensic Science Center. Exposure to VX, a potent nerve gas, can lead to paralysis and respiratory failure. Sulfur mustard is a blister agent that was dispersed in aerosol form during World War I to incapacitate troops and contaminate areas to discourage entry. Few facilities can test chemical vapor detectors with actual chemical warfare agents. Typically, tests are performed using surrogates such as common cleaning products. The sensor was exposed to VX and sulfur mustard at concentrations of 520 parts per billion (ppb) and 90 ppm, respectively. These values can be compared to the median lethal concentrations of 450 ppb for VX and 25 ppm for sulfur mustard, which correspond to percutaneous (passing through the skin) vapor exposure for 30 minutes.

The results of the experiments can be rendered in a single, three-dimensional graph representing all 13 signatures. The data for each chemical align along a trajectory that originates at the zero concentration state and ultimately terminates at the saturation state. "Clearly, the sensor can identify the different chemicals it was trained to detect throughout the concentration ranges we looked at," says Hart. "Although



In this three-dimensional graph, each colored line represents a distinct chemical signature detected by the Livermore sensor over a range of concentrations. All lines originate from a common point (right) representing the zero concentration state of pure air. The specific agent concentrations for the chemical warfare agents VX, sulfur mustard, and thiodiglycol (a sulfur mustard precursor) correspond to approximately 50 percent of the lethal concentration levels for human-skin exposure.

discriminating from among many different compounds may be challenging, we are confident that the signals for chemicals of interest will predominate." *The Analyst* article represented the first published report of detecting a chemical warfare agent using a sensor array of polymer-coated microcantilevers.

Transitioning from the Laboratory

Any new sensor design must successfully transition from the laboratory with its carefully controlled environment to applications in the real world where users will have little or no control over the operating environment. "If a sensor is used in an enclosed environment where the humidity and temperature are constant, then compensation for these effects is straightforward," says Loui. Because temperature, humidity, and other meteorological conditions can vary widely outdoors, the Livermore sensor was also tested for 24-hour periods in an external environment.

In addition, a viable sensor for use in a real-world application must balance advanced capabilities with the requirements for a particular assignment. "If reliable trace detection at the parts-per-trillion level is absolutely required or we need to analyze gas samples with dozens or more constituents, then a traditional mass spectrometer is needed," says Loui. "MEMS-based sensors will likely never achieve these capabilities. However, sensors such as our cantilever array are suitable for applications in which a detector's size, power economy, and unit cost are of paramount importance. For these applications, the mass spectrometer would be less than ideal because of its bulky size and hefty price tag of $10,000 and more."

Loui is developing a mathematical model that explains how environmental factors contribute to the sensor's response. The goal is for the sensor to "smell" past these interfering phenomena and still respond to the chemical vapor of interest. The model incorporates various physical, chemical, and mechanical properties to determine how the device, in particular the microcantilever coatings, is affected by environmental changes.

Many Possible Applications

The Livermore sensor could potentially be used in a variety of applications because it is small, robust, and sensitive; needs only commercial support electronics; and can be mass-produced. The device is ideal for autonomous operation for long periods. Example applications include environmental and industrial monitoring, such as for chemical leaks in manufacturing plants or storage facilities. Of particular interest to homeland security and defense experts is the speedy detection of gases that could indicate the onset of a chemical warfare attack. Soldiers could carry handheld sensors, or even miniaturized lapel pins, that warn of a chemical agent in the environment. "The sensors could also be scattered around a military base and run autonomously, sensing for incoming plumes of chemicals," says Hart. In addition, the sensors could prove useful as explosives "sniffers" in airports and as spoilage indicators for the food industry.

A novel application for the sensor is as a disease diagnostic. Hart notes that the presence of specific chemicals is associated with certain disease states. A microcantilever-based device could become an important diagnostic tool in analyzing the breath of a patient and searching for a telltale molecule indicative of a particular disease. In 2008, a team of University of California at Davis students captured top awards in two business plan competitions with a plan based on the Livermore microcantilever technology. Their business plan featured a device that would allow people with diabetes to test their blood-sugar levels by blowing into a small handheld device. This technology could offer an alternative to glucose monitoring, which requires that people prick their fingers to draw a blood sample, in some cases several times a day.

The current Livermore prototype cannot be used to detect biological agents, which typically do not exist in the vapor phase. However, a sensor designed to detect biowarfare agents in water would be possible if the microcantilevers' plastic coatings were replaced with nucleotides or antibodies. Previously, Livermore researchers have demonstrated

The Livermore sensor easily fits in one hand. Researchers are working to shrink the electronics even more, so the sensor can be incorporated into a cell phone or even a lapel pin.

biological applications for sensors using microcantilevers covered with biomolecules.

Looking to the Future

The team is exploring additional features for the chemical sensor such as onboard data storage and wireless transmission capabilities. Hart has discussed with government agencies the feasibility of designing a wireless sensor that would permit units to "talk" to one another as well as to a control server. Such a network could aid in mapping the presence of a chemical vapor of interest. Another feature being explored incorporates a resistive heater into each microcantilever to hasten desorption when the microcantilevers are purged, which would lessen the approximate 2-minute interval between readings in the current design. A transition to coatings of cross-linked polymers for greater mechanical stability is also planned. In addition, Hart is reviewing the feasibility of using nanocantilevers measuring only a few hundred nanometers wide because of their potential sensitivity to tiny amounts of material. Finally, Hart is investigating how the Livermore sensor might be incorporated into a cell phone that would also have sensors for detecting radiation and biological warfare agents. A network of these advanced cell phones could quickly warn, identify, and determine the extent of a contamination.

A prototype offshoot of the device is part of a Livermore effort to develop tiny, rugged sensors that could be embedded in every U.S. nuclear warhead and last for decades. The sensors could potentially be used to detect and measure gas molecules, such as volatile organic compounds and water vapor, which might impede the performance of critical warhead components. Embedded sensors could provide information currently obtainable only through disassembly. Such devices might make possible for the first time "persistent surveillance"—continuous monitoring of every weapon and practically instantaneous detection of anomalies. (See *S&TR,* July/August 2008, pp. 12–19.) "Our goal is a sensor that can 'smell' the outgassing of tiny amounts of chemicals," says Loui, who is the lead investigator on adapting the sensor to stockpile surveillance. "If successful, we could have warheads capable of indicating when an internal problem exists."

"We want to move the new sensor technology out in the field as rapidly as possible," says Hart. The Laboratory has received several inquiries from industrial firms interested in licensing the technology. With mass production of the device in sight, Hart is hopeful Livermore's sensor will become ubiquitous throughout industry as well as a dependable element of chemical warfare detection and defense—in essence a trusty network of "smoke detectors" for toxic chemicals.

—Arnie Heller

Key Words: chemical weapon, detector, Forensic Science Center, microcantilever, microelectromechanical systems (MEMS), National Consortium for Measurement and Signatures Intelligence Research, polyolefin, sensor, sulfur mustard, VX.

For further information contact Brad Hart (925) 423-1970 (hart14@llnl.gov).