Chemical Weapons Can't Evade This Lab

Livermore's Forensic Science Center is certified to support the treaty that bans chemical weapons.

LAWRENCE Livermore has been among the leaders in supporting national and world efforts to detect chemical weapons and thwart their proliferation. In February, the international Organisation for the Prohibition of Chemical Weapons (OPCW) certified Livermore's Forensic Science Center (FSC) to support its chemical weapons inspections.

"Chemical weapons are a growing threat to the security of the U.S. and its allies," says Jeff Richardson, deputy program leader for the Proliferation Prevention and Arms Control Program in Livermore's Nonproliferation, Arms Control, and International Security Directorate. "Putting the capabilities of FSC to work in the effort to prevent the spread of chemical weapons is one more way the Laboratory can contribute to national and international security."

In light of its demonstrated capabilities to analyze and characterize unique samples, FSC was selected by the U.S. State Department in 2000 to become the second U.S. laboratory to support the OPCW, pending certification by the OPCW. (The other facility is the U.S. Army's Edgewood Chemical and Biological Forensic Analytical Center in Maryland.) Under the terms of the Chemical Weapons Convention (CWC), the international agreement banning chemical weapons that the OPCW oversees, all inspection samples must be analyzed at two OPCW-designated laboratories. In addition, the U.S. Senate has mandated that all samples obtained within the U.S. must be tested in the U.S. so that proprietary information belonging to American chemical manufacturers will be protected. (See the box on p. 8.)

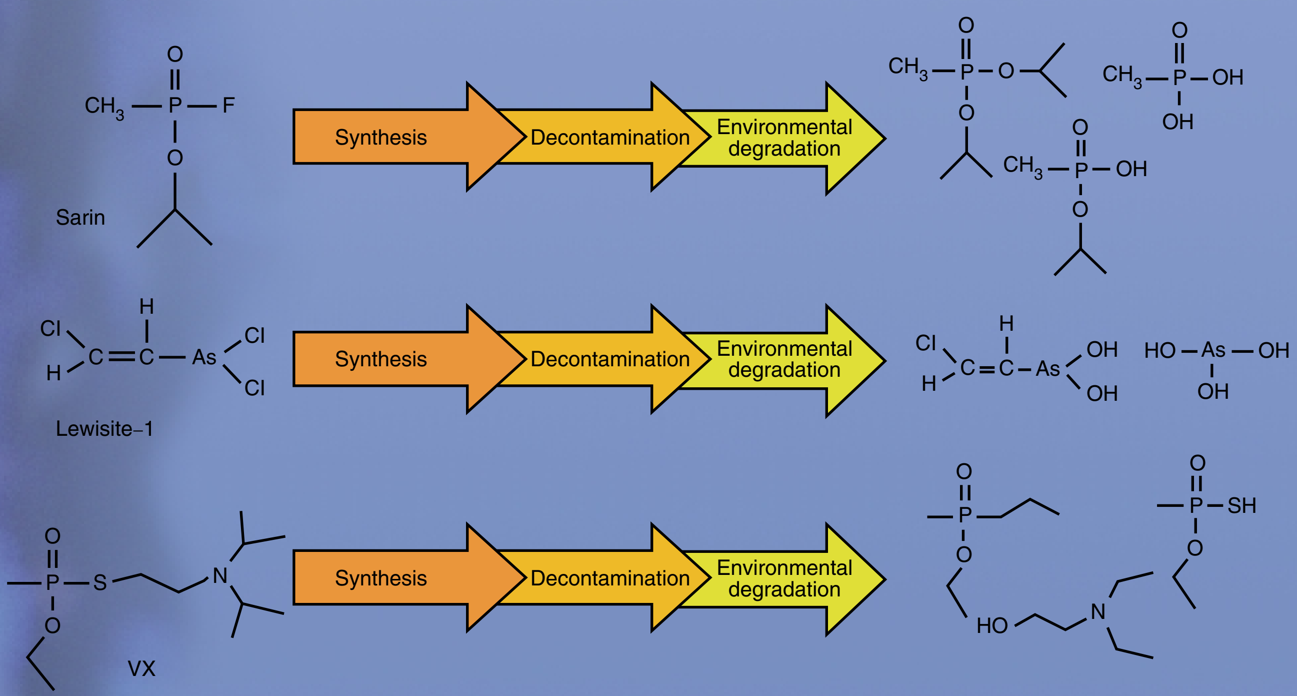
According to Livermore chemist and principal investigator Armando Alcaraz, FSC was originally selected by the State Department because of the Laboratory's advanced environmental controls and physical security and FSC's demonstrated capabilities in detecting and analyzing minute traces of unknown materials. Alcaraz also cites FSC's previous participation in international exercises to detect chemical agents and FSC chemists' work with colleagues at Edgewood. (See the box on p. 11.)

Livermore Joins Select Group

FSC joins about 15 other laboratories around the world that have been certified by the OPCW. The purpose of these laboratories is to test samples collected by OPCW inspectors from chemical plants and other sites to determine whether the samples contain scheduled chemicals (chemical weapons or their precursors) or their decomposition products. (The annex to the CWC has three schedules, or lists, of banned and monitored compounds: Schedule 1 compounds are the most toxic, and Schedule 3 compounds are less toxic or are dual-use chemicals.) To date, no samples have been officially collected from any sites. The only samples examined by the OPCW-certified laboratories have been those prepared for proficiency tests and exercises.

Livermore achieved its OPCW certification by passing three grueling proficiency tests. The tests involved the analysis and characterization of samples containing combinations of extremely dilute amounts of chemical warfare agents, precursor chemicals, and decomposition products as well as other chemicals included to complicate or obfuscate the analysis. The tests that led to accreditation took place in November 2001, April 2002, and October 2002. Different OPCW-designated laboratories formulated the test samples and graded FSC findings.

The proficiency tests used samples that simulated those the OPCW



Laboratories certified by the Organisation for the Prohibition of Chemical Weapons must be capable of detecting minute amounts of chemical warfare agents, precursor compounds, and their decomposition products.

Test samples occasionally contain emulsions of different layers, with each layer containing suspected chemical warfare agents, precursors, or decontamination products.

inspectors might send to Livermore for analysis. The test samples typically consisted of soil, a water-based solution, and an organic-based solution, each contained in sealed glass vials. One test sample looked like milk, but in reality was an emulsion of aqueous and organic phases, each containing suspected products.

Each vial contained one or more scheduled compounds that had to be identified. For each test, the Livermore team was given 15 days to analyze the samples and report its findings.

Background information was also provided on the simulated inspection scenario of the tests. For example, in one scenario, the note claimed that the samples were taken during an inspection of a foreign pesticide plant. Inspectors had supposedly obtained the samples from different locations around the plant, including soil from outside the plant because it might contain degradation products from illicit manufacturing of chemical weapons.

Analysis Plan Is Well-Rehearsed

Thanks to the three proficiency tests, the Livermore team of chemists now has a well-rehearsed plan for analyzing an OPCW sample. A large conference room is transformed into a "war room." Whiteboards on the walls are covered with flow diagrams and notes about possible compounds contained in the samples. "It's a pretty intense time, but we're very focused, and we have outstanding teamwork," says Hugh Gregg, coprincipal investigator.

During the 15 days of analysis, Rich Whipple prepares samples and Alcaraz and Gregg lead the analysis, aided by Robert Maxwell and Greg Klunder. Andy Vance, John Reynolds, and Phil Pagoria synthesize compounds used to confirm the presence of suspected compounds, and Tuijauna Mitchell-Hall provides quality control.

A large conference room is transformed into a "war room" for discussions and posting flow diagrams and notes about possible chemical warfare compounds contained in samples.

Alcaraz emphasizes that team members follow all applicable safety and security requirements for analyzing and synthesizing dilute chemical agents. In some cases, he says, the solvent is more hazardous than the target compounds because any chemical warfare compounds in the samples have been diluted to extremely low concentrations.

The team uses a variety of analytical techniques, including gas chromatography, mass spectrometry, atomic emission detection, gas chromatograph flame photometric detection, chemiluminescense, infrared spectrometry, liquid chromatography, inductively coupled plasma mass spectrometry, nuclear magnetic resonance, and capillary electrophoreses. With three nuclear magnetic resonance machines and more than 12 gas chromatograph–based analyzers at their disposal, the team has one of the world's best-equipped labs to analyze exceedingly small amounts of material.

"We use all the instruments because each gives us unique information," says Gregg. For example, FSC recently acquired a gas chromatograph capable of infrared detection because it yields structural information about a compound. The OPCW requires that at least two different analytical techniques be used for positive identification, and the Livermore team strives to obtain confirmation from three or four different techniques.

The workhorse instrument is the gas chromatograph–mass spectrometer (GC–MS), which can detect ultratrace quantities of organic compounds weighing a billionth of a gram or less. A few microliters of a sample are injected into the GC–MS, where the sample is vaporized and the sample components are separated and analyzed.

Looking for Suspicious Elements

One of the most important first steps in analyzing OPCW samples is doing quick screens with the GC–MS and element-specific detectors to look for a few key elements that indicate the possible presence of chemical warfare compounds. For example, lewisite contains arsenic, sarin contains phosphorous and fluorine, and VX contains phosphorous, nitrogen, and sulfur.

Alcaraz notes that just as important as finding actual chemical warfare agents is finding the chemicals that are associated with their manufacture. Many precursors are listed on Schedule 1 because they are unique to the manufacture of chemical weapons. The CWC list of scheduled chemicals includes tens of thousands of chemicals, most of which have never been synthesized or characterized but are thought to be as deadly as their well-known analogs. Identifying these "designer" agents is an extremely difficult but necessary part of the job.

Breakdown products of chemical agents also qualify as "smoking guns." The chemists must keep in mind the possible products that could be found, for example, in the wastes from a chemical or pesticide manufacturing plant. And the team must anticipate the products that might result from

(a) Chemist Armando Alcaraz logs in a proficiency test sample. (b) Chemist Bob Maxwell holds a sample in a tube that will be placed in a nuclear magnetic resonance instrument (in background). (c) Alcaraz injects a microliter of sample into a gas chromatograph–infrared spectrometer system. (d) Chemist Hugh Gregg uses solid-phase extraction cartridges to clean a sample of hydrocarbon compounds that might mask a chemical warfare agent.

decontamination procedures, as might happen if someone used bleach or another strong oxidizer to eliminate traces of illegal chemical agent manufacture. The team must also consider degradation products resulting from environmental factors such as sunlight and rain. Some chemical agents are stable while others, such as the nerve agent sarin, break down easily.

Whipple notes that the sample solutions may also contain agents, such as dirty diesel oil, that mask the target compounds present in vanishingly small quantities. In one case, when the diesel oil was carefully removed, the chemists found trace amounts of a chemical warfare agent precursor.

Watching for Red Herrings

Finally, the team must be ready to locate and identify any of thousands of possible compounds added to the samples as red herrings. These compounds are not found in any chemistry reference because they were created just for the test in an effort to fool the analysts. They are often similar or identical in molecular weight and elemental composition to well-known chemical warfare compounds.

“Many compounds will look like a Schedule 1 compound, but if we report it as such, we fail the test,” says Vance. One such compound contained sulfur, phosphorous, and nitrogen, good indicators of a nerve agent, and the molecular weight was in the ballpark for a well-known nerve agent. With the aid of multiple syntheses and nuclear magnetic resonance analysis, the team figured out its structure, which was different from that of any nerve agent (and therefore not scheduled). The compound had been made by an OPCW laboratory to confuse chemists analyzing the sample.

Vance notes that OPCW has provided a database of thousands of compounds, complete with molecular weight, structure, and what the GC–MS spectrum should look like. In addition, the GC–MS will suggest the identity of a compound based on the 2,000 to 3,000 compounds in its

Chemical Weapons and the Treaty That Bans Them

The Convention on the Prohibition of the Development, Production, Stockpiling, and Use of Chemical Weapons and on Their Destruction (commonly known as the Chemical Weapons Convention, or CWC) defines chemical weapons as toxic chemicals and their precursors. Chemical and biological weapons have been referred to as the poor man’s nuclear weapons. This is particularly true of chemical weapons, which are easily and affordably manufactured and can inflict mass casualties.

Chemical weapons are often grouped by their biological response. Nerve agents include sarin, soman, and VX; blister agents include mustard gas and lewisite; vomiting agents include diphenylcyanoarsine; and tearing agents include CS gas.

Many chemical warfare agents are similar to common industrial chemicals. In fact, troops during World War I used several unmodified industrial chemicals as weapons. For example, German troops opened canisters of chlorine and let winds disseminate the gas. Nerve agents, developed just before and during World War II, are related chemically to the organophosphorous insecticides and are among the most deadly: With some of them, one drop on the skin can cause respiratory failure and death.

The Geneva Protocol prohibiting the use of chemical weapons in warfare was signed in 1925. Several nations, including the U.S., signed with a reservation forswearing only the first use of the weapons. The U.S. ratified the protocol in 1975.

Chemical weapons were used by Italy in Ethiopia and by Japan in Manchuria and China prior to World War II, but no chemical weapons were deliberately employed by the Allies or the Axis powers during the war. Iraq used chemical weapons, including mustard gas, during the Iran–Iraq conflict of 1982 to 1987. Evidence indicates that it used chemical weapons within its own boundaries in 1988 when it killed about 5,000 Kurds in Halabja with a combination of mustard gas and the nerve gases sarin, tabun, and VX.

Until 1985, virtually all uses of chemical weapons had been as tactical weapons by nations. Then, in a terrorist attack, the Japanese cult Aum Shinrikyo released sarin gas in a Tokyo subway, killing 12 people and injuring more than 5,000. Currently, thousands of toxic chemicals could be used as chemical weapons. Many can be manufactured in existing chemical plants or individual laboratories.

Classes of chemical warfare agents.

1 Nerve	2 Blister	3 Vomiting	4 Tearing
• Sarin (GB)	• Mustard (HD)	• Diphenylcyanoarsine	• Chloracetophenone
• Soman	• Lewisite (L-1)	• Adamsite (DM)	• Chloropicrin (PS)
• VX, Vx	• Nitrogen mustard	• Diphenylchloroarsine	• CS

library. However, the instrument is not foolproof because more than one compound can have the same molecular weight and elemental composition.

As a result, once the team suspects the presence of a particular compound, it must obtain a reference sample, either from its storehouse of 500 to 1,000 stock chemicals or by synthesizing the compound. Either way, the reference is then screened by the same instruments to make sure it gives identical readings.

Vance points out that synthesizing the suspect chemicals poses no health or safety risk because chemists work in a special hood and use gloves. More importantly, they only synthesize extremely small amounts of material, never exceeding a concentration of 1 milligram per milliliter and a total of 10 milliliters of solution.

Because the GC–MS separates compounds, the synthesis chemists aren't concerned about purifying their product, which saves valuable time. They also aren't concerned about yield. "If we have only fractions of a microgram, the GC–MS will find it," Vance says. "The hard part is that doing things as fast as possible and not caring about yield is counter to my experience on other projects in which the focus was on maximizing yield and purity."

Aiding the synthesis effort are parallel synthesis techniques. A parallel synthesis instrument can perform up to 20 simultaneous reactions in temperature- and atmosphere-controlled reaction vessels. Vance can make multiple compounds that meet molecular weight and elemental composition requirements and then analyze all of them to find one that matches.

Alcaraz notes that as Day 15 approaches, "We feel the pressure. We're always thinking, 'Did we miss something?'" To answer that question, the team invites other Livermore chemists to a meeting about three to four days before the deadline to

The only toxin to exist naturally is ricin, made from the ubiquitous castor bean plant. British authorities found traces of ricin, for which there is no antidote, in a raid on a London apartment in January 2003. Instructions for making ricin have been found in the possession of several suspected terrorists and fighters in Chechnya.

CWC Extends Globally

The CWC is a global treaty that bans the development, production, stockpiling, and use of chemical weapons. Parties to the treaty are obligated to destroy their chemical weapons and production facilities within a specified period of time. They also must not assist other states in the production of chemical weapons. (The U.S. has been destroying its stockpile of chemical weapons at a cost of many billions of dollars.)

CWC negotiations began in 1980 as part of the United Nations Conference on Disarmament. The CWC went into effect on April 29, 1997, four days after the U.S. signed. Currently, more than 145 nations have signed the treaty, although nations such as Iraq and North Korea have not.

The CWC places controls on toxic chemicals and their precursors, which are listed on three schedules according to their toxicity, military and commercial utility, and risk. Schedule 1 lists military agents with no or low commercial use, such as nerve agents and mustards as well as their direct precursors. Schedule 2 lists high-risk precursors and toxic chemicals that are not produced in large quantities for commercial use. Schedule 3 lists dual-use chemicals, some of which have been used as weapons or precursors but which are produced in large quantities for purposes not prohibited by the CWC. The treaty allows states to produce an aggregate of 1 metric ton or less of Schedule 1 chemicals for research, medical, pharmaceutical, and protective purposes.

The CWC is the first arms control and nonproliferation treaty to widely affect the private sector. Although the U.S. does not manufacture chemical weapons, it does manufacture, use, import, and export a number of dual-use chemicals that could be used to produce chemical weapons. U.S. companies engaged in activities involving certain chemicals may be required to submit reports to the Department of Commerce and may be subject to inspections.

The CWC is implemented by the Organisation for the Prohibition of Chemical Weapons (OPCW), which is headquartered in The Hague, Netherlands. The OPCW has almost 500 employees, including a multinational corps of inspectors. Any treaty party that suspects another signatory of conducting activities prohibited by the CWC has the right to ask for a challenge inspection of the suspect site. The analysis of samples may be done at the suspect site, but samples can also be transferred to approved OPCW laboratories for additional analysis.

When the U.S. Senate ratified the CWC, it implemented a mandate, Condition 18, which states that no sample taken on U.S. soil shall leave the U.S. for analysis during an OPCW inspection. However, it is an OPCW requirement that two OPCW-accredited laboratories must analyze the samples and provide independent correlation. The two accredited U.S. laboratories are the U.S. Army's Edgewood Chemical and Biological Forensic Analytical Center and Livermore's Forensic Science Center.

review its analysis work and give comments and suggestions. The meeting, says Gregg, shows that "this is a real team effort, not just one person."

Finally, the team sends its report, complete with instrument readouts and flow diagrams, to OPCW headquarters, where it is forwarded to a certified lab for grading. Gregg notes that OPCW has taken Livermore's report format and made it the standard for all designated laboratories.

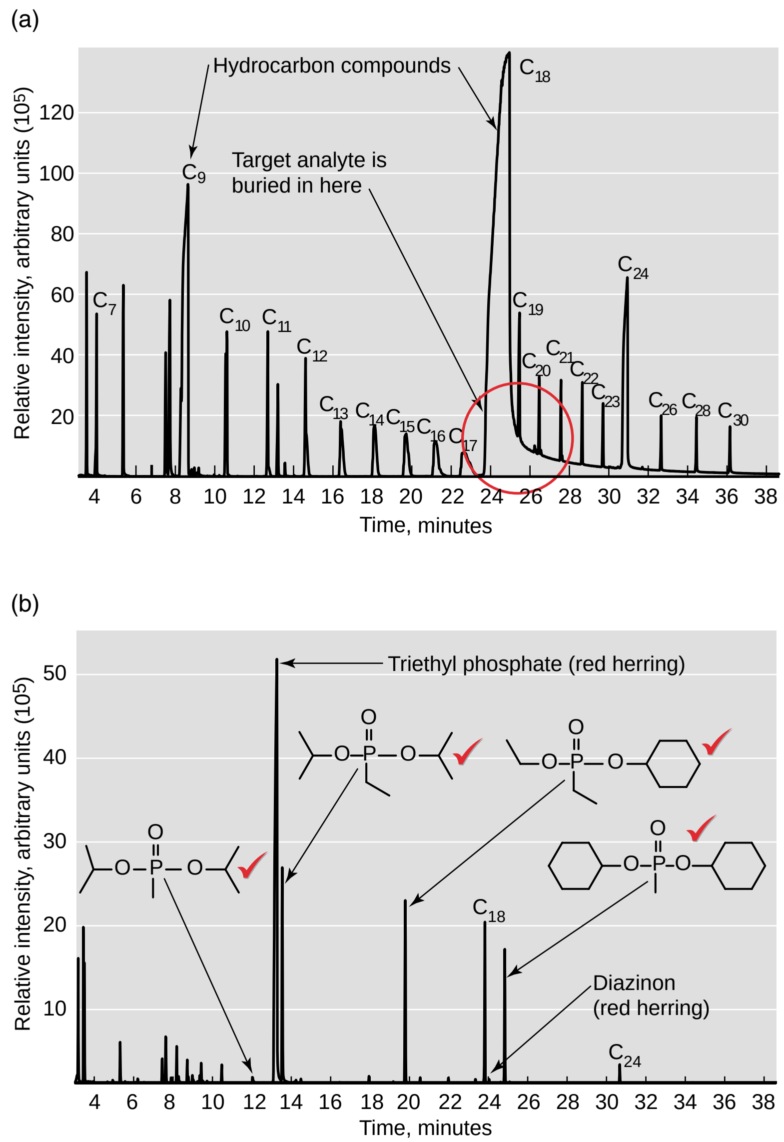
First Exercise Tests System

In early February, the team participated in OPCW's first exercise designed to test all the procedures related to using the designated laboratories, including procedures for shipping and analyzing authentic samples. Not part of the proficiency tests, the exercise involved samples from a mock inspection site in Singapore that had been sent to OPCW headquarters in The Hague, Netherlands. OPCW added a quality control sample and a blank solution and placed them in a specially designed stainless steel case for transfer by commercial shippers to participating laboratories in Livermore, South Africa, and Britain.

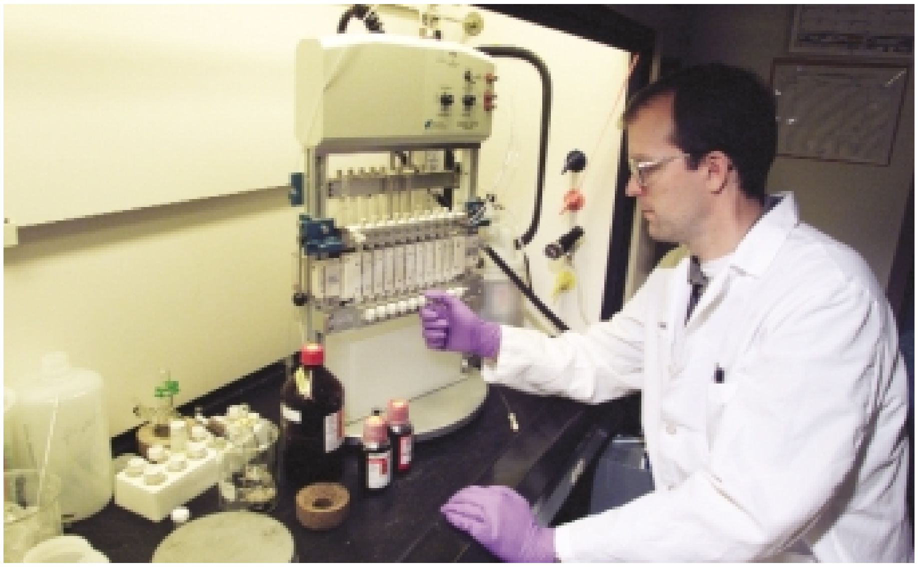
Before sending the samples to Livermore, OPCW notified the U.S. State Department, which notified Alcaraz and Gregg. Upon hearing from Alcaraz that FSC was ready, the OPCW sent the samples to Livermore. "We wanted to discover any customs and shipping problems that could come up with officially labeled samples from OPCW," says Alcaraz. Because of paperwork and customs issues both in Europe and at the Los Angeles airport, the samples arrived a week later than expected.

An OPCW inspector from Zimbabwe was on hand at Livermore to verify the samples' intact seals and weights. OPCW rules also allow a representative from the nation where the samples are taken to monitor the analysis. As with the proficiency tests, the Livermore team had 15 days to send in their analysis but finished the task in just one week. This sample handling exercise was beneficial to OPCW and the U.S. Potential and actual pitfalls in collecting, transporting, and analyzing authentic samples and reporting the results have been identified and are being addressed.

Alcaraz anticipates that FSC may receive samples for analysis several times a year from OPCW inspections.



(a) This chromatograph of a sample was produced by a gas chromatograph–mass spectrometer. Hydrocarbons could be masking trace amounts of chemical weapon agents. (b) Once the hydrocarbons are removed, the analysis reveals the presence of a compound that is a precursor to a chemical warfare agent.



Chemist Andy Vance uses parallel synthesis techniques to quickly prepare reference compounds and try to match them to what the team suspects are chemical warfare agents, precursors, or decontamination products.

Chemical Weapons Work Is Part of FSC Expertise

The laboratory certified by the Organisation for the Prohibition of Chemical Weapons (OPCW) operates as part of Livermore's Forensic Science Center (FSC). Founded in 1991, FSC offers a comprehensive range of analytical expertise to counter terrorism, aid domestic law enforcement and homeland security, and verify compliance with international treaties and agreements.

The center's human and technological resources have made it among the leading facilities for collecting and analyzing virtually any kind of evidence, some of it no greater than a few billionths of a gram. FSC has expertise in ultratrace chemical and isotopic analyses of nuclear, inorganic, organic (chemical warfare agents, illegal drugs, explosives), and biological materials (toxins, DNA).

FSC also develops new technologies for detecting and characterizing the source of weapons materials. A major effort is adapting forensic analysis technologies for field use. For example, FSC scientists have shrunk the standard gas chromatograph–mass spectrometer so it fits inside a wheeled suitcase. (See *S&TR*, April 2002, pp. 11–18.) When necessary, the center draws upon experts in Livermore's Chemistry and Materials Science and Nonproliferation, Arms Control, and International Security directorates.

Government and law enforcement agencies call upon FSC for analyses beyond the capabilities of their in-house laboratories and for interpreting samples demanding unusually high-quality forensic analyses. In 1998, the Federal Bureau of Investigation named FSC as the bureau's West Coast support laboratory. As part of the OPCW accreditation process, FSC in November 2001 obtained an International Organization for Standardization certification in the field of chemical testing by the American Association for Laboratory Accreditation.

Samples could contain just about any suspect material, including water, soil, gasket material, and even chips of concrete. As with the test samples, real samples will be diluted by inspectors before they are forwarded to an OPCW-designated laboratory.

In the meantime, the team is doing data validation work for the OPCW-developed libraries of scheduled chemicals. These libraries are used by inspectors with portable GC–MS instruments in the field and by designated laboratories performing analyses. Livermore chemists are evaluating the spectral data to make sure they are accurate. In addition, FSC, like all OPCW-designated laboratories, is expected to maintain high scores (at least two "A's" and a "B" on yearly proficiency tests) to keep its certification.

Alcaraz notes that FSC would like to make its chemical warfare agent analysis resources available to other government agencies. For example, he suggests the center could aid homeland security by providing technical support to first responders who suspect chemical agents. Agencies such as local health departments and the Environmental Protection Agency do not have expertise identifying chemical warfare agents, he says. Fortunately, Lawrence Livermore is certified to do the job.

—*Arnie Heller*

Key Words: chemical weapons, Chemical Weapons Convention (CWC), Forensic Science Center (FSC), Organisation for the Prohibition of Chemical Weapons (OPCW).

For further information contact Armando Alcaraz (925) 423-6889 (alcaraz1@llnl.gov).