

## Monitoring at Chemical Agent Disposal Facilities



Committee on Monitoring at Chemical Agent Disposal Facilities, National Research Council

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# MONITORING AT CHEMICAL AGENT DISPOSAL FACILITIES

Committee on Monitoring at Chemical Agent Disposal Facilities

Board on Army Science and Technology

Division on Engineering and Physical Sciences

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## Preface

The Committee on Monitoring at Chemical Agent Disposal Facilities was appointed by the National Research Council (NRC) in July 2004 to review the instrumentation systems and practices for monitoring airborne chemical agent levels associated with chemical weapons demilitarization and stockpile storage facilities operated by the U.S. Army's Chemical Materials Agency (CMA). The committee was also charged with reviewing how the new chemical agent airborne exposure limits recommended by the Centers for Disease Control and Prevention (CDC) in 2003 and 2004 and implemented by the CMA in 2005 would impact the effectiveness of the Army's current agent monitoring and whether new applicable monitoring technologies were available and could be effectively incorporated into the CMA's overall airborne chemical agent monitoring strategies. The committee's statement of task is presented in Chapter 1, along with an account of the committee's activities. Biographies of the committee members' professional activities are presented in Appendix A.

Airborne chemical agent monitoring systems at CMA weapons disposal and storage facilities serve multiple purposes: to warn workers of unexpected levels of agents within their workplaces, to ensure that workers are not exposed to persistent unhealthful concentrations of airborne agent, and to document any significant passage of airborne agent across facility boundaries that might harm the general population or the environment. The agent concentrations routinely monitored by the CMA are extremely low, with fence-line monitoring limits based on the new CDC recommendations ranging from 0.003 to 0.00005 parts per billion by volume, depending on the chemical agent. The detection of very low chemical agent concentrations within air masses containing much larger levels of other industrial and environmental contaminants that can interfere with chemical agent detection makes the CMA's monitoring tasks very challenging.

Assessing the utility of both the current CMA monitoring technology and the future usefulness of potential advanced monitoring technology required the committee's membership to understand a full range of modern analytical chemistry measurement techniques and instrumentation; the chemical, physical, and toxicological properties of the relevant chemical agents; and the operational characteristics of the CMA weapons disposal and storage facilities. In considering these topics, the committee reviewed the scientific literature, and it queried and was subsequently briefed by many capable scientists and engineers associated with the CMA, the CDC, and other relevant federal agencies. The committee also drew heavily on relevant recent NRC reports addressing chemical weapons demilitarization issues, including *Occupational Health and Workplace Monitoring at Chemical Agent Disposal Facilities*;<sup>1</sup> *Evaluation of Chemical Events at Army Chemical Agent Disposal Facilities*;<sup>2</sup> and *Impact of Revised Airborne Exposure Limits on Non-Stockpile Chemical Materiel Program Activities*.<sup>3</sup> The committee benefited from the experience and insights of members who participated in the preparation of each of these prior reports.

This study was conducted under the auspices of the NRC's Board on Army Science and Technology (BAST). The chair acknowledges the strong support of the BAST

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<sup>1</sup>NRC (National Research Council). 2001. *Occupational Health and Workplace Monitoring at Chemical Agent Disposal Facilities*. Washington, D.C.: National Academy Press.

<sup>2</sup>NRC. 2002. *Evaluation of Chemical Events at Army Chemical Agent Disposal Facilities*. Washington, D.C.: The National Academies Press.

<sup>3</sup>NRC. 2005. *Impact of Revised Airborne Exposure Limits on Non-Stockpile Chemical Materiel Program Activities*. Washington, D.C.: The National Academies Press.



director, Bruce A. Braun, and the project's study director, Margaret N. Novack. Valuable research and editorial assistance were provided by BAST staff members, Harrison Pannella, James Myska, and Nia Johnson. Detra Bodrick-Shorter provided outstanding logistical support. Finally, the committee's vice chair, Jeffrey Steinfeld, and each of the committee members contributed critical content and innovative insights that inform this report, and they willingly shared

the demanding writing and reviewing tasks in a highly professional and collegial manner.

Charles E. Kolb, *Chair*  
Committee on Monitoring at  
Chemical Agent Disposal Facilities

## Acknowledgment of Reviewers

This report has been reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise, in accordance with procedures approved by the National Research Council's Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the institution in making its published report as sound as possible and to ensure that the report meets institutional standards for objectivity, evidence, and responsiveness to the study charge. The review comments and draft manuscript remain confidential to protect the integrity of the deliberative process. We wish to thank the following individuals for their review of this report:

Gene H. Dyer, San Rafael, California

B. John Garrick, National Academy of Engineering,  
Laguna, California

Gary S. Groenewold, Idaho National Engineering and  
Environmental Laboratory, Idaho Falls

Eugene R. Kennedy, National Institute for Occupational  
Safety and Health, Cincinnati, Ohio

Sanford S. Leffingwell, HLM Consultants, Auburn,  
Georgia

Although the reviewers listed above have provided many constructive comments and suggestions, they were not asked to endorse the conclusions or recommendations, nor did they see the final draft of the report before its release. The review of this report was overseen by Royce W. Murray, University of North Carolina. Appointed by the National Research Council, he was responsible for making certain that an independent examination of this report was carried out in accordance with institutional procedures and that all review comments were carefully considered. Responsibility for the final content of this report rests entirely with the authoring committee and the institution.



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## Acronyms and Abbreviations

|         |  |                |   |
|---------|--|----------------|---|
| ABCDF   | Aberdeen Chemical Agent Disposal Facility (Maryland) | DOAS           | differential optical absorption spectroscopy  |
| ACAMS   | Automatic Continuous Air Monitoring System           | DPE            | demilitarization protective ensemble          |
| A/DAM   | Agilent/Dynatherm agent monitor                      | EI             | electron impact                               |
| AEGL    | acute exposure guideline level                       | EPA            | Environmental Protection Agency               |
| AEL     | airborne exposure limit                              | FM             | frequency modulation                          |
| AFRL    | Air Force Research Laboratory                        | FPD            | flame photometric detector                    |
| ANCDF   | Anniston Chemical Agent Disposal Facility (Alabama)  | FT-IR          | Fourier transform infrared                    |
| ASC     | allowable stack concentration                        | GA             | tabun (a nerve agent)                         |
| BAST    | Board on Army Science and Technology                 | GB             | sarin (a nerve agent)                         |
| BMI     | Bretby Maintainability Index                         | GC             | gas chromatography                            |
| CAIS    | chemical agent identification set(s)                 | GF             | cyclosarin                                    |
| CB      | carbon black composite                               | GPL            | general population limit                      |
| CCD     | charge-coupled device                                | H              | sulfur mustard                                |
| CDC     | Centers for Disease Control and Prevention           | HD             | sulfur mustard (distilled)                    |
| CE      | capillary electrophoresis                            | hr             | hour  |
| CI      | chemical ionization                                  | HS             | sulfur mustard                                |
| CIMS    | chemical ionization mass spectrometry                | HT             | sulfur mustard, T-mustard mixture             |
| Cl      | chlorine   | HV             | high volume                                   |
| CMA     | (U.S. Army) Chemical Materials Agency                | IDLH           | immediately dangerous to life and health      |
| CRDS    | cavity ringdown spectroscopy                         | IMS            | ion mobility spectrometry                     |
| cts     | counts   | JACADS         | Johnston Atoll Chemical Agent Disposal System |
| CWA     | chemical warfare agent                               | JCAD           | Joint Chemical Agent Detector                 |
| CWC     | Chemical Weapons Convention                          | LED            | light-emitting diode                          |
| CWIC    | Chemical Warfare Indicating Chromophore              | LOD            | limit of detection                            |
| 1,3-DNB | dinitrobenzene                                       | LOQ            | limit of quantification                       |
| 2,4-DNT | dinitrotoluene                                       | m <sup>3</sup> | cubic meter                                   |
| DAAMS   | Depot Area Air Monitoring System                     | MACT           | maximum achievable control technology         |
| DART    | Direct Analysis in Real-Time                         | MEMS           | microelectromechanical systems                |
| DCD     | Deseret Chemical Depot (Utah)                        | mg             | milligram                                     |
| DESI    | desorption electrospray ionization                   |                |   |
| DIMP    | diisopropylmethylphosphonate                         |                |   |
| DMMP    | dimethyl methylphosphonate                           |                |   |

|                   |   |          |   |
|-------------------|---|----------|---|
| mg/m <sup>3</sup> | milligram per cubic meter   | QA/QC    | quality assurance/quality control                             |
| MINICAMS          | Miniature Chemical Agent Monitoring System                                  | QP       | quality plant   |
| mm                | millimeter  | QRA      | quantitative risk assessment                                  |
| MPGC              | multipass gas cell  | RCRA     | Resource Conservation and Recovery Act                        |
| MPI               | Max Planck Institute  | RDX      | cyclotrimethylenetrinitramine                                 |
| MSD               | mass selective detector   | RMSEC    | root-mean-square error of calibration                         |
| ms/ms             | mass spectrometry/mass spectrometry   | RMSEP    | root-mean-square error of prediction                          |
| mW                | milliwatt   | s        | second  |
| m/z               | mass-to-charge ratio  | S        | sulfur  |
| 4-NT              | mononitroaromatics (incomplete nitration product in the production of TNT)  | S/N      | signal-to-noise ratio   |
| NaOH              | sodium hydroxide  | SAIC     | Science Applications International Corporation                |
| NCAR              | National Center for Atmospheric Research                                    | SCD      | sulfur chemiluminescence detector                             |
| nm                | nanometer   | SEL      | source emission limit   |
| NO <sub>2</sub>   | nitric oxide  | SERS     | surface-enhanced Raman scattering                             |
| NOAA              | National Oceanic and Atmospheric Administration                             | Si       | silicon   |
| NRC               | National Research Council   | SMI      | storage monitoring and inspection                             |
| NRT               | near real time  | SO       | sulfur oxide  |
|                   |   | STEL     | short-term exposure limit                                     |
| OP/FT-IR          | open-path Fourier transform infrared  | THF      | tetrahydrofolate  |
| OPH               | organic phosphate hydrolase   | TNT      | trinitrotoluene   |
| O,S-DMP           | O,S-diethyl methylphosphonothiolate (a by-product in the manufacture of VX) | TOCDF    | Tooele Chemical Agent Disposal Facility (Utah)                |
| OSHA              | Occupational Safety and Health Administration                               | TWA      | time-weighted average   |
|                   |   | UMCDF    | Umatilla Chemical Agent Disposal Facility (Oregon)            |
| P&A               | precision and accuracy  | USACHPPM | U.S. Army Center for Health Promotion and Preventive Medicine |
| PAS               | photoacoustic spectroscopy  | UV       | ultraviolet   |
| PBCDF             | Pine Bluff Chemical Agent Disposal Facility (Arkansas)                      | VLSI     | very large scale integrated circuit                           |
| PDARS             | process data acquisition and reporting system                               | VX       | a nerve agent   |
| PFPD              | pulsed flame photometric detector   | WPL      | worker population limit                                       |
| pg                | picogram  | XSD      | halogen-selective detector                                    |
| PMT               | photomultiplier tube  |          |   |
| ppb               | parts per billion   |          |   |
| ppbv              | parts per billion by volume   |          |   |
| PPE               | personal protective equipment   |          |   |
| ppt               | parts per trillion  |          |   |

## Glossary

**absorbance.**  $\text{Log}_{10}$  (transmitted light intensity/incident light intensity).

**absorptivity.** Absorbance divided by path length times concentration.

**adsorbent.** Material that causes a species in the supernatant vapor (e.g., air) or liquid phase to bind to its surface.

**analyte.** The chemical species being measured; a substance whose identity or chemical composition is to be determined by chemical analysis.

**array detector.** A photoelectric detector in which a large number of photosensitive elements are distributed, usually in regularly spaced lines over a rectangular area.

**charge-coupled device (CCD).** Chip that stores information in the form of charge packets in an array of closely spaced capacitors. Many video recorders and digital cameras employ CCD chips.

**chemical ionization.** The process of ionizing a molecule through a chemical or charge-transfer reaction.

**electropherogram.** A record of the variation with time of the signal from a detector used in capillary electrophoresis.

**electrospray source.** A dilute solution of an analyte in a solvent, forced through a capillary at high voltage. Charged particles are formed and the solvent evaporates, leaving a charged analyte.

**library.** A collection, for example, of sensors (a sensor library), or a database of reference spectra.

**Mie scattering.** Light scattering by particles with diameters that are greater than or similar to the wavelength of the

scattered radiation, but are too small to yield specular or diffuse reflection.

**multipass gas cell.** A cell in which light that has entered the cell is repeatedly reflected through a gaseous sample before it emerges to the detector.

**near real time.** <15 minute response (*see* real time).

**neural network.** A data-processing algorithm in which input data are multiplied by a series of weighting factors selected so that an association between the input pattern and a desired output pattern is “learned” by the software. From <http://www.webopedia.com/>: “A type of artificial intelligence that attempts to imitate the way a human brain works. Rather than using a digital model, in which all computations manipulate zeros and ones, a neural network works by creating connections between *processing elements*, the computer equivalent of neurons. The organization and weights of the connections determine the output.”

**number density.** A measure of concentration, molecules per cubic centimeter.

**partition.** The process in which an ensemble of molecules is distributed between two generally immiscible phases, e.g., oil and water. The partition coefficient is the ratio of the final concentrations in each of the two phases.

**polarity.** The distribution of charge within a molecule.

**preconcentration.** Collection of analyte, typically obtained by drawing air over an adsorbent so as to increase the amount of analyte available for a measurement.

**proton affinity.** The negative of the enthalpy change resulting from adding a proton ( $\text{H}^+$  ion) to a molecule.

**quantum efficiency (fluorescence yield).** The ratio of the amount of light reradiated by a molecule following absorption of light, generally on a photon-per-photon basis.

**Raman scattering.** Scattering of light by a sample in which the optical frequency is changed by an amount corresponding to a vibrational transition of a molecule in the sample.

**Rayleigh scattering.** Scattering of light from particles that are usually much smaller than the wavelength of the light. The incident and scattered light have the same optical frequency.

**real time.** 1 to 10 second response (*see* near real time).

**retroreflector.** Precision mirror that reflects a beam of light exactly back to its source.

**sensor surface functionality.** The chemical structure at the surface of a sensing material.

**sensor training.** A type of calibration in which responses are collected from sensors exposed to a series of analytes and are used to create a pattern-recognition algorithm, also called a *classifier*.

**solvatochromic fluorescence indicator.** A fluorescent dye that changes its intensity or color when placed in environments of different polarity.

**transferable classifier.** A computer-based pattern-recognition algorithm that can be used on multiple sensor arrays (*see* sensor training).

## Executive Summary

This report from the National Research Council's (NRC's) Committee on Monitoring at Chemical Agent Disposal Facilities was requested by the U.S. Army for purposes of advising its Chemical Materials Agency (CMA) about the status of analytical instrumentation technology and systems suitable for monitoring airborne chemical warfare agents at chemical weapons disposal and storage facilities.

The CMA is currently operating six chemical weapons disposal facilities located at storage sites in the continental United States and has completed the disposal of weapons once stored overseas. Disposal facilities at two U.S. sites are still in the design stage. To date, just over a third of the chemical agent in the original stockpile has been destroyed. It is likely that disposal operations will not be completed until 2012 or later.

The committee was charged to review both the current monitoring systems used for airborne agent detection at CMA facilities and to investigate the applicability and availability of innovative new technologies. It was also tasked with considering how the regulatory requirements for airborne agent monitoring, particularly the new chemical agent airborne exposure limits (AELs) recommended by the Centers for Disease Control and Prevention (CDC) in 2003 and 2004 and implemented by the CMA in 2005, would impact the effectiveness of the CMA's current agent monitoring procedures, and whether any applicable new monitoring technologies that are available could be effectively incorporated into the CMA's overall chemical agent monitoring strategies. A review of the CMA's chemical weapons demilitarization challenge, an account of the committee's activities, and the committee's statement of task are presented in Chapter 1.

### CHEMICAL AGENT MONITORING CHALLENGE

In order to protect its workforce as well as both the general public and the environment near its facilities, the CMA monitors airborne chemical agents at exceedingly low levels.

Through the use of near-real-time (NRT) instruments, the ambient air inside much of each facility is monitored for concentrations of agents not to exceed (depending on the type of agent) 0.4 to 0.0008 parts per billion by volume (ppbv) every 15 minutes or less. The purpose of this monitoring is to warn workers if unexpected levels of agent have penetrated areas in which protective gear is normally not required. Exhaust emissions in the pollution abatement system and the exhaust stack are also monitored for agents by NRT instruments at the source emission limits (SELs), which are only modestly higher levels than those acceptable for the ambient air in the facility.

In addition, using sample collection and analysis techniques, historical monitoring is performed within the facility, in accordance with the new AELs, at agent concentration levels that are 3 to 10 times lower (depending on the type of agent) than the levels for plant air NRT monitors in order to ensure that the workers are not exposed to very low but persistent levels of agent. These same sampling and laboratory analysis systems are used as confirmation monitors to determine if adjacent NRT monitor alarms are actually caused by a chemical agent or another pollutant. Finally, the sampling and analysis method is also used at CMA facility perimeters to monitor at extremely low agent levels that, based on the new CDC recommendations, range from 0.003 to 0.00005 ppbv (depending on the chemical agent). Such monitoring is intended to ensure that no significant level of agent migrates over the fence line of a CMA facility and affects the nearby public or environment.

The need to detect very low chemical agent concentrations within air masses that may also contain much higher levels of other industrial and environmental contaminants that can interfere with chemical agent detection makes the CMA's monitoring tasks very challenging. In order to assess this challenge, the committee reviewed the CMA's chemical agent monitoring requirements, the chemical and physical properties of the stockpiled chemical agents, and the former (1988) and current (2003/2004) chemical agent AELs; its

review is presented in Chapter 2. The committee does find that the CDC's newly promulgated AEL, the short-term exposure limit (STEL), is an appropriate basis for NRT monitoring at CMA facilities, since it ensures worker protection. The committee recommends that the Army continue to use STELs as the basis for NRT monitoring.

In order to develop the framework for evaluating the performance of the current CMA airborne agent monitoring systems and for evaluating potential novel agent monitoring technology, the committee reviewed the science of analytical trace gas detection and quantification and the components of trace gas monitoring systems. Its review is presented in Chapter 3.

## CURRENT AIRBORNE AGENT MONITORING SYSTEMS

A detailed review of the CMA's current agent monitoring instruments, systems, and practices that focuses on the challenges posed by the CDC's new 2003/2004 AELs is presented in Chapter 4. The committee concurs with previous NRC reports that frequent NRT false-positive alarms have been a persistent problem (NRC, 1994, 1999, 2001, 2002).<sup>1</sup> It reviewed some recent NRT monitoring data which indicated that the CMA has made progress in reducing, but has not eliminated this problem. The committee finds that the Army has indeed made progress in reducing NRT false positives, but notes that this type of false-positive alarm will likely continue to be a problem, particularly for the nerve agent VX. The committee also finds that an increased frequency of false positives may be experienced for historical monitoring sample-collection-and-laboratory-analysis systems as the CMA implementation of the lower 2003/2004 AEL levels for historical monitoring of the workplace and at the fence line continues. Despite some problems with false-positive measurements, the committee also finds that the current NRT monitoring and the monitoring technology for sampling and laboratory analysis appear to provide sufficient airborne agent monitoring capability to afford adequate protection to workers, the general public, and the environment. However, given that the disposal operations will be ongoing for some years, at least until 2012 and perhaps beyond, the committee recommends that the CMA should consider a wider range of incremental improvements to the Automatic Continuous Air Monitoring System (ACAMS), the Miniature Chemical Agent Manufacturing System (MINICAMS), and the Depot Area Air Monitoring System (DAAMS) to allow these monitoring systems to better monitor at the CDC's 2003/2004 AELs. Some technologies

that deserve consideration by the CMA are shown in Chapter 4.

The committee also notes that the CMA has historically set the NRT alarm levels at some fraction of the relevant AEL or SEL, with the goal of ensuring a statistical alarm response rate of 95 percent or better when agent is present at the AEL or SEL. The committee finds that neither the CMA's plans to possibly set alarm levels at 1.0 AEL/SEL nor the inclination of state regulators to specify alarm levels of 0.2 AEL may be optimal. The committee recommends that the Army should consider continuing to use alarm levels that ensure that all properly operated and maintained NRT monitors at a given site have at least a 95 percent probability of sounding an alarm any time the true agent concentration in an area being monitored exceeds 1.00 STEL. The committee's analyses and recent operational experience indicate that this can often be achieved with an alarm level of ~0.5 AEL/SEL, and that such a setting will tend to reduce false-positive alarms without greatly enhancing the probability of false-negative measurements.

## ADVANCED CHEMICAL AGENT MONITORING TECHNOLOGY

After reviewing the performance of the current airborne monitoring technology used in CMA facilities, in Chapter 5 the committee reviews newer trace gas monitoring technologies that might be applicable for airborne agent monitoring in CMA facilities. Here it focuses on technologies that might provide real-time (~1 s) agent detection capability without sacrificing too much sensitivity or specificity. The committee examined two vibrational spectroscopy technologies: Fourier transform infrared (FT-IR) spectroscopy, employed in either an open-path or a folded multipass gas cell configuration, and surface-enhanced Raman scattering (SERS). The committee finds that FT-IR spectroscopy will likely have limited utility because its limited sensitivity for the relevant chemical agents makes real-time detection at STEL or lower AELs problematic. FT-IR might be configured to detect concentrated agent plumes encountered near large emission sources that contain agent concentrations of 0.05 mg/m<sup>3</sup> (~4 to 8 ppb) or higher. Likewise, SERS is not likely to allow real-time agent detection at STEL levels and does not promise significant advantages over current NRT monitors.

The committee did, however, find that chemical ionization mass spectrometry (CIMS) is a highly sensitive trace gas detection technique, widely deployed in atmospheric chemistry research studies to measure a variety of trace gases, and that it is potentially capable of measuring the stockpiled chemical agents at concentrations well below STEL levels in real time. The committee recommends that the Army should investigate whether present CIMS instrumentation could be immediately used to detect chemical agents at the immediately dangerous to life and health (IDLH) limit in real time. The use of negative ions as a

<sup>1</sup>False-positive alarms refer to situations in which an agent concentration above a specified level is indicated by an alarm but is not true; false-negative alarms refer to situations in which a specified level is exceeded but no alarm is sounded.



precursor should be investigated to improve selectivity. Adaptation of one of the research-grade atmospheric field instruments for real-time detection between the STEL and the general population limit (GPL) for each relevant agent should be considered.

The committee also examined the rapidly evolving field of chemical sensor arrays but concluded that, while they might soon be useful in detecting agents at the relatively high, IDLH limit, the development time required for these sensor arrays to work reliably at the STEL or lower AELs is probably too long to impact the CMA's chemical weapons disposal program. The committee also finds that since the federal government is currently the only obvious customer for chemical agent detection at STEL or lower levels, the commercial development of sensors with this capability is unlikely without direct federal support.

## CHEMICAL AGENT MONITORING SUMMARY

The committee also reviewed specific requirements for airborne agent monitoring and analyzed event scenarios in which releases of chemical agents in CMA's weapons disposal or storage facilities might motivate the development and adoption of new airborne agent monitoring technologies to supplement the CMA's existing agent monitoring systems. The results of this review and analyses are presented in Chapter 6.

Consistent with previous NRC reports (NRC, 1999, 2001), the committee finds that the current airborne agent monitoring systems are adequate to safely protect the chemical demilitarization workforce, the public, and the environment, although potential incremental improvements that enhance sensitivity and specificity to reduce the rate of false-positive alarms and/or cycle times might improve plant efficiency and safety. The committee recommends that continued incremental improvements in the current airborne chemical agent monitoring systems at chemical stockpile storage and demilitarization sites, as discussed in Chapter 4 of this report, should be pursued by the Army.

On the basis of its evaluations of the potential agent release scenarios coupled with information on the probable detection capabilities of the newer agent monitoring technologies, the committee finds that disposal facility unpack areas might sustain agent releases, possibly including agents other than the one that its NRT monitors are set up to detect for the current agent disposal campaign. The committee recommends that the Army should analyze whether the addition of real-time and/or multiagent monitoring in the unpack area of chemical demilitarization facilities that process multiple munitions would significantly reduce risk to workers who unpack and stage munitions for processing. If the risk analysis indicates a significant enhancement of

worker safety, the Army should investigate whether other, shorter response time and/or multiagent deployment modes for current NRT monitors or the development and/or procurement of real-time, multiagent monitors based on innovative technology are feasible and practical.

The committee also finds that, to pose an acute risk to the public, the atmospheric release of sufficient chemical agent vapor or aerosol would require a major accident, almost certainly involving explosion and/or fire. The ability to confirm dispersion model predictions that an agent plume has penetrated the depot boundary and threatens the public or to track the agent plume would require fast-response monitors operating at levels between the STEL and the IDLH that are either widely dispersed or are mounted on a suitable ground or air mobile platform. The committee recommends that the Army and other relevant stakeholders should assess whether public protection would be significantly enhanced by the development and deployment of dispersed fixed or portable fast-response agent sensors or the development of a mobile fast-response agent sensor platform capable of detecting and tracking a large release plume.

The committee finds that open- or folded-path FT-IR and CIMS technology have some promise for providing enhanced, fast-response chemical agent monitoring capability to chemical weapons storage and demilitarization facilities. However, the committee recommends that the Army should only deploy advanced chemical agent monitoring equipment after a thorough risk/benefit analysis shows that the risk reduction to the workforce and/or public justifies the monetary and opportunity costs. If worker or public risk reduction analyses indicate significant benefit at acceptable cost from deployment of fast-response, multiagent monitoring capabilities, systems using FT-IR or, more likely, CIMS should be considered.

An overview of the committee's findings and recommendations is presented above. Detailed findings and recommendations associated with the data, references, and analyses that support them are presented in Chapters 2, 4, 5, and 6. All of the findings and recommendations are also grouped together in Chapter 7.

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- NRC (National Research Council). 1994. Review of Monitoring Activities Within the Army Chemical Stockpile Disposal Program. Washington, D.C.: National Academy Press.
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# 1

## Introduction

### REPORT GENESIS

Under the direction of the U.S. Army's Chemical Materials Agency (CMA), the nation is engaged in the destruction of its stockpile of chemical weapons. In order to protect the health of the demilitarization workforce and destroy these weapons safely, it is necessary to monitor extremely minute levels of airborne chemical agent at sites where these weapons are stored, when transporting them between a storage area and the adjacent demilitarization (disposal) facility, and in the ambient air and process disposal streams of the disposal facilities. Protection of the public living and/or working near the stockpile storage areas and disposal facilities requires the monitoring of even more minute levels of airborne chemical agents at the fence lines of the storage areas and disposal facilities.

At the Army's request, the National Research Council (NRC) previously examined the chemical agent monitoring systems that have been deployed at the Army's chemical disposal facilities, and provided advice about methods to improve the currently deployed systems and about the potential role of new technology to supplement the current system (NRC, 1994, 2001). The NRC also evaluated the performance of and identified some operational weaknesses in the currently deployed monitoring systems (NRC, 1999) and analyzed the role that these weaknesses played in a small number of chemical events that resulted in the release of small amounts (less than 50 mg per event) of chemical agent into the ambient air (NRC, 2002).

In July 2004, the Army asked the NRC to reevaluate the operation of the airborne chemical monitoring systems deployed at its chemical agent disposal facilities and to investigate whether new measurement technology that could supplement current capabilities is available or quickly achievable. The reevaluation is partially motivated by the adoption of new, lower airborne exposure limits (AELs) for the chemical agents present in the stockpile and by the CMA's need to reevaluate and redefine its monitoring

policies in response to this change (U.S. Army, 2004). The study was also motivated by congressional interest in the possibility of using additional fence-line or community monitoring technologies that might provide extra warning for the public in the event of a significant release of agent from a storage area or disposal facility (National Defense Authorization Act for Fiscal Year 2004, enacted November 24, 2003 (Public Law 108-136), sec. 1056). The full statement of task for this study appears later in this chapter.

### CHEMICAL DEMILITARIZATION CHALLENGE

During the Cold War, the United States produced and stockpiled 31,496 tons of unitary nerve agents (sarin (GB) and VX) and blister (sulfur mustard (H, HD, and HT)) chemical agents. These agents were loaded into millions of individual munitions or, alternatively, stored in bulk containers. These weapons are now obsolete and have been banned by the Chemical Weapons Convention (CWC), an international treaty that was ratified by the U.S. Congress in 1997. Earlier, in 1985, the Congress had mandated (Department of Defense Authorization Act of 1986, enacted in November 1985 (Public Law 99-145)) that the Army institute a sustained program to destroy some elements of the chemical weapons stockpile, and in 1992 it extended this mandate to require the destruction of the entire stockpile (Arms Non-Proliferation Act of 1992, enacted in 1991 (Public Law 102-484)). The CWC requires that its signatory nations destroy their entire chemical weapons stockpiles by April 29, 2012.

From 1990 to 2000, the Army incinerated 2,031 tons of chemical agents and the associated energetic materials in 412,732 munitions and containers that had been stored at Johnston Atoll, southwest of Hawaii, at the Johnston Atoll Chemical Agent Disposal System (NRC, 2002). The remaining chemical agent stockpile was dispersed among eight continental U.S. storage sites, six that have agent loaded into munitions and two that have only bulk containers of agent. The locations, types, and percentage of stockpiled agent and

the range of munitions and containers that were stored at each of these stockpile sites are shown in Figure 1-1.

The Deseret Chemical Depot (DCD) in Tooele, Utah, which originally contained 44.5 percent of the chemical agent stockpiled at the eight continental sites, started agent destruction with a second-generation incineration facility, the Tooele Chemical Agent Disposal Facility (TOCDF), in 1996. TOCDF completed destruction of 50 percent of the DCD stockpile in the summer of 2004. Three third-generation incinerator facilities are now operational. The Anniston Chemical Agent Disposal Facility (ANCDF) started operations in Anniston, Alabama, in 2003; the Umatilla Chemical Agent Disposal Facility (UMCDF) in Umatilla, Oregon, began operations in 2004; and the Pine Bluff Chemical Agent Disposal Facility (PBCDF) in Pine Bluff, Arkansas, began agent operation in March 2005.

The Army has constructed chemical neutralization (hydrolysis) facilities at the two stockpile sites that store only single types of agent in ton containers—one at the Edgewood portion of Aberdeen Proving Ground, Maryland, where sulfur mustard (distilled) (HD) was stored, and the other in Newport, Indiana, where VX is stored. The Aberdeen facility started operations in 2003 and completed agent destruction in early 2005. The Newport facility began operations in May 2005. Designs for neutralization facilities to destroy the stockpiled chemical agent and associated munitions at

Pueblo, Colorado, and the Blue Grass facility in Lexington, Kentucky, are currently being developed. Early in 2005, the CMA announced that one-third of the initial chemical agent stockpile had been destroyed.

### COMMITTEE COMPOSITION AND STATEMENT OF TASK

The NRC established the Committee on Monitoring at Chemical Agent Disposal Facilities in mid-July 2004 at the request of the CMA. The committee's members included experts in analytical, physical, and environmental chemistry, toxicology, chemical process engineering, human factors engineering, industrial safety and operations, and chemical weapons storage and handling (see Appendix A for biosketches of the committee members).

The committee's statement of task, prepared for the NRC by the Army, was as follows:

The committee will review and comment on the status of the Army's and systems contractors' monitoring capabilities for chemical airborne agents. Specifically, the committee will:

- Examine existing and applicable new monitoring technologies for sensitivity, selectivity, response time, reproducibility, and reliability and determine the extent to which these technologies can be incorporated into overall

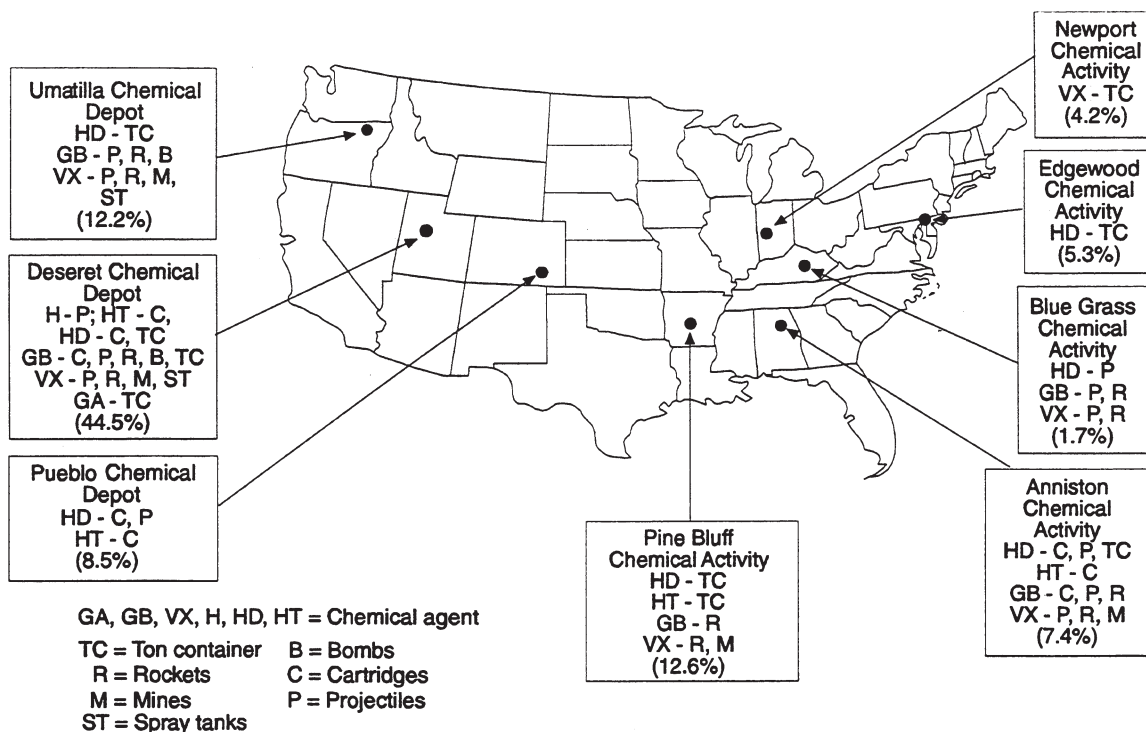


FIGURE 1-1 Location and original size (percentage of original chemical agent stockpile) of eight continental U.S. storage sites. NOTE: Of the more than 30,000 tons of agent that were in the original stockpile, only a relatively small amount was GA (tabun). Only two 1-ton containers of pure GA and two 1-ton containers of thickened GA were present in the stockpile at Deseret Chemical Depot in Utah. SOURCE: OTA, 1992.

program monitoring strategies, particularly for the purposes of process verification, permit compliance, upset conditions, and disposal management. This shall include an examination of sampling techniques and protocols.

- Assess how regulatory standards for emissions, including the CDC's [Centers for Disease Control and Prevention's] recently promulgated nerve agent and proposed mustard agent airborne exposure limits and the US EPA's [Environmental Protection Agency's] Maximum Achievable Control Technology (MACT) rule, are addressed by available monitoring technologies. If existing technology is unable to meet new standards, assess the maturity of each feasible monitoring technology in terms of scope, facility constraints, and schedule to implementation.

## COMMITTEE ACTIVITIES

The committee met in Washington, D.C. (September 2004); Edgewood, Maryland (October 2004); Washington, D.C. (November 2004); and Irvine, California (January 2005) (see Appendix B). Presentations were received from the following organizations:

- U.S. Army Chemical Materials Agency (CMA);
- U.S. Army Center for Health Promotion and Preventive Medicine;
- Department of Defense's Joint Program Executive Office for Chemical and Biological Defense;
- U.S. Army Research, Development, and Engineering Command—Edgewood Chemical Biological Center;
- Scientific Applications International Corporation;
- General Physics Corporation; and
- Battelle Memorial Institute.

At these meetings, the committee also held discussions in closed session during which the chemical agent monitoring requirements at chemical agent disposal facilities were analyzed and text for the report was drafted. Committee members and the committee's NRC study director also visited chemical agent disposal facilities at Pine Bluff Arsenal in December 2004 to review on-site agent monitoring systems and discuss agent detection challenges and procedures with the monitoring branch and laboratory staff at this site. A committee member and several NRC staff also attended the CMA-sponsored "Technologies for Chemical Agent Detection Workshop" that was held in Washington, D.C., on August 24, 2004.

## REPORT ROADMAP

The challenge of monitoring airborne chemical agents accurately, specifically, and quickly at the parts-per-trillion level and below is discussed in Chapter 2 of this report, along with the relevant chemical and physical properties of

chemical agents, recently revised AELs, and the related monitoring action levels adopted by the CMA. Chapter 3 reviews the general properties of trace chemical measurements and measurement systems. It also addresses the requirements for the operation of an effective and reliable monitoring system in the industrial environment in and around a chemical agent disposal facility.

The analytical instruments, sampling components, and integrated monitoring systems currently used to detect airborne chemical agents at storage and disposal facilities are reviewed in Chapter 4. The chapter also contains an analysis of the strengths and weaknesses of these monitoring systems and discusses potential improvements to the systems. Chapter 5 reviews a range of highly sensitive trace chemical detection technologies, currently in use or under development, that might be adapted for use in chemical agent disposal facilities.

Potential agent release scenarios in which enhanced monitoring might improve worker safety and promote safe agent disposal or better protect the public and the environment around chemical agent disposal facilities are developed and presented in Chapter 6. The ability of improved versions of the current monitoring technologies or supplemental new monitoring instruments to realize these potential benefits is evaluated. The technical maturity, regulatory compatibility, and potential commercial availability of either improved versions of current systems or supplemental new instrument technology are also evaluated. The committee's findings and recommendations, presented throughout the report, are collected in Chapter 7. In addition to the committee biosketches and activities presented in Appendixes A and B, respectively, Appendix C contains the text of an amendment proposed in 2003 concerning the sense of the U.S. Senate on deployment of systems for monitoring of airborne chemical agent at U.S. chemical stockpile disposal sites.

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- NRC (National Research Council). 1994. Review of Monitoring Activities Within the Army Chemical Stockpile Disposal Program. Washington, D.C.: National Academy Press.
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## 2

# Chemical Agent Monitoring Challenges

### CHEMICAL DEMILITARIZATION AND STORAGE MONITORING REQUIREMENTS

Monitoring for airborne chemical agents in storage and demilitarization operations is accomplished through three types of activities:

- *Historical monitoring* is employed to ensure and document that there are no ongoing emissions of chemical agents from either storage areas or demilitarization processing activities to which unprotected workers or the public might be exposed. Historical monitoring is typically employed in areas where chemical agents would not be expected, and thus, a positive finding would initiate an investigation to determine the nature and source of contamination.
- *Near-real-time (NRT) monitoring* (i.e., having a response time of approximately 3 to 15 minutes) is employed in areas where the presence of agent is likely or possible, and is conducted to ensure that any exposures to which stockpile and/or demilitarization process workers might be subjected during their employment at the facility do not exceed recommended guidelines for worker protection. NRT monitoring is also employed to detect process upset conditions.
- *Confirmation monitoring* is employed to validate or invalidate a positive result from another monitoring system (historical or NRT). It may involve multiple sampling and analytical methods.

Both NRT and historical monitoring systems are employed to ensure that regulatory (permit) requirements for demilitarization operating facilities are met.

The underlying technology for all current monitoring systems in use at demilitarization facilities is essentially the same, in that these systems rely on gas chromatographic techniques. The monitoring strategies employed by the Army have, in general, served to provide assurance that chemical

demilitarization has proceeded in a manner that is protective of human health and the environment. Even so, false-positive results—especially with NRT monitoring—have been problematic at times because they have triggered unnecessary disruptions in the destruction process and delays in program execution. False-positive monitoring results remain a challenge for improving the overall monitoring program. For additional information on this topic, see the NRC report *Evaluation of Chemical Events at Army Chemical Agent Disposal Facilities* (NRC, 2002).

### CHEMICAL AGENT PROPERTIES

The chemical weapons stockpile includes both nerve and blister agents. Nerve agents include VX, tabun (GA), and sarin (GB). All of the nerve agents are organophosphonate compounds. Blister agents include various formulations of sulfur mustard (H, HD, and HT) and arsenicals such as lewisite. Figure 2-1 shows the chemical structures of the major components of the chemical weapons stockpile, and Table 2-1 gives some of their physical properties.

Physical properties that are particularly relevant to monitoring strategies are the vapor pressures and volatility values, because they indicate the relative ability of chemicals to become airborne. VX and the three types of mustard agent are essentially nonvolatile, in that they are thousands of times less volatile than water is. For either VX or the three types of mustard agent to be detected outside chemical demilitarization facilities or storage areas at potentially harmful concentrations would require a catastrophic event such as an explosion (in Chapter 6, see the section entitled “Potential Major Release Scenarios” for discussion). Agent GB, which is more volatile (somewhat similar to water) than the other agents, could conceivably be transported off-site in the event of a significant spill in a storage area that went undetected for an extended period of time.



TABLE 2-1 Physical Properties of Chemical Warfare Agents

| Agent Characteristic                       | Nerve Agents  |  | Blister (Mustard) Agents <sup>a</sup>               |   |
|--|---|--|---|---|
|  | GB (Sarin)  | VX   | HD  | HT  |
| Chemical formula                           | (CH <sub>3</sub> ) <sub>2</sub> CHO(CH <sub>3</sub> ) FPO | C <sub>11</sub> H <sub>26</sub> NO <sub>2</sub> PS | (ClCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> S | 60% HD, 40% ((ClCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> SCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O and homologues |
| CAS Registry No.                           | 107-44-8  | 50782-69-9   | 505-60-2  | N/A   |
| Molecular weight                           | 140.10  | 267.38   | 159.08  | (mixture—188.96 based on 60/40 weight percent)  |
| Boiling point, °C                          | 150 (extrapolated)  | 292 (extrapolated)                                 | 218   | No constant boiling point   |
| Freezing point, °C                         | -56   | <-51   | 14.5  | 0 to 1.3  |
| Vapor pressure, mm Hg @ 25 °C              | 2.48  | 0.0009   | 0.106   | 0.077 × 10 <sup>-2</sup> (calculated based on Raoult's law equation and 60 weight percent HD and 40 weight percent HT)          |
| Volatility, mg/m <sup>3</sup>              | 3,370 at 0 °C<br>187,000 at 25 °C                         | 12.6 at 25 °C                                      | 75 at 0 °C (solid)<br>906 at 20 °C (liquid)         | 783 at 25 °C  |
| Surface tension, dynes/cm                  | 26.5 at 20 °C   | 32.0 at 20 °C                                      | 43.2 at 20 °C<br>42.4 at 25 °C <sup>b</sup>         | 42.0 at 25 °C   |
| Kinematic viscosity, cS                    | 1.28 at 25 °C   | 12.26 at 20 °C                                     | 3.52 at 20 °C                                       | 6.50 at 20 °C   |
| Liquid density, g/cm <sup>3</sup> at 20 °C | 1.0887  | 1.0083   | 1.27  | 1.26  |
| Latent heat of vaporization, cal/g         | 82.9  | 71.8   | 94.3  | N/A   |
| Solubility, g/L H <sub>2</sub> O at 25 °C  | Completely miscible                                       | 50 at 21.5 °C                                      | 0.92  | Similar to HD   |
| Heat of combustion (cal/g)                 | 5,600   | 8,300  | 4,500   | N/A   |

<sup>a</sup>The blister agents are labeled HD and HT. The active ingredient in all of these agents is bis(2-chloroethyl) sulfide, (ClCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>S. HD, called distilled mustard, is nominally pure bis(2-chloroethyl) sulfide. H, often called Levenstein mustard, is approximately 70% bis(2-chloroethyl) sulfide and 30% impurities, which tend to be polysulfides such as (ClCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>S<sub>n</sub>. HT is a mixture of ca. 60% (ClCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>S and 40% ((ClCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>SCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O.

<sup>b</sup>The surface tension of HD at both 20°C and 25°C is shown to allow the reader to compare the surface tensions of HD and HT under the same physical conditions, while also allowing a general comparison of the surface tensions of nerve agents and blister agents across constant physical conditions.

SOURCE: Based on data provided to the NRC Committee to Assess Designs for the Pueblo and Blue Grass Chemical Agent Destruction Pilot Plants and on data from Abercrombie, 2003.

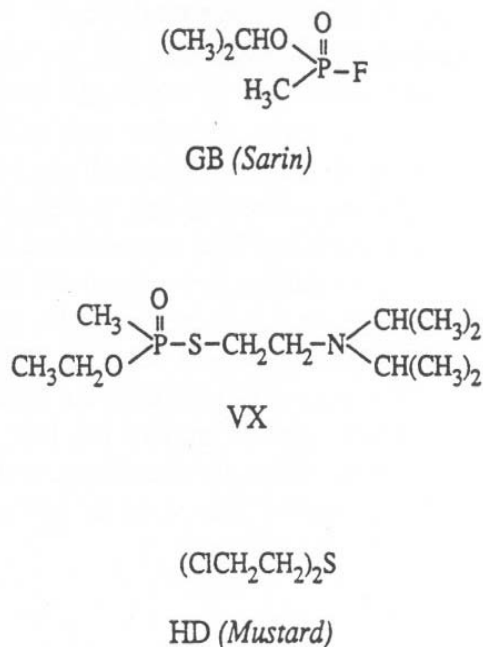


FIGURE 2-1 Chemical structures of the major components of the U.S. chemical weapons stockpile. SOURCE: Adapted from original source. NRC, 2001a.

## CHEMICAL AGENT AIRBORNE EXPOSURE LIMITS AND DEMILITARIZATION ACTION LEVELS

### General Definitions

Airborne exposure limits (AELs) for the nerve agents and sulfur mustard were established by the Centers for Disease Control and Prevention (CDC) in 1988 (Federal Register, 1988). The Army adopted the 1988 AELs as exposure standards to protect workers in demilitarization facilities and the surrounding general populations. The AELs accepted by the Army were a worker population limit (WPL)<sup>1</sup> and a general population limit (GPL) for sarin (GB), tabun (GA),<sup>2</sup> VX, and sulfur mustard (distilled) (HD). Their initial values are presented in Table 2-2, along with newer values proposed in 2003/2004. The 1988 AELs were used as the basis for the Army's monitoring program from the commencement of

<sup>1</sup>In 1988, the CDC identified the AELs as "Control Limits" for the general population and workers. The Army termed the worker control limit as a "TWA" (time-weighted average) but has used the value as a ceiling value limit. WPL is used here for the 1988 TWA for ease of comparison with new WPLs.

<sup>2</sup>As noted in Figure 1-1 in this report, there is a relatively small amount of GA in the stockpile.

TABLE 2-2 CDC's 1988 and 2003/2004 Recommended Airborne Exposure Limits (AELs) and U.S. EPA/NRC 2003 Acute Exposure Guideline Levels (AELs) for GA, GB, VX, and HD

| Airborne Exposure Limits                        |                        | GA/GB  | VX  | HD   |
|---|------------------------|--|---|--|
| Type of Limit                                   | Year of Recommendation | (mg/m <sup>3</sup><br>(1 mg/m <sup>3</sup> = 160 ppb)) | (mg/m <sup>3</sup><br>(1 mg/m <sup>3</sup> = 84 ppb)) | (mg/m <sup>3</sup><br>(1 mg/m <sup>3</sup> = 141 ppb)) |
| Short-term exposure limit (STEL)                | 1988                   | N/A  | N/A   | N/A  |
|   | 2003/2004              | 1 × 10 <sup>-4</sup>                                   | 1 × 10 <sup>-5</sup>                                  | 3 × 10 <sup>-3</sup>                                   |
| Worker population limit (WPL)                   | 1988                   | 1 × 10 <sup>-4</sup>                                   | 1 × 10 <sup>-5</sup>                                  | 3 × 10 <sup>-3</sup>                                   |
|   | 2003/2004              | 3 × 10 <sup>-5</sup>                                   | 1 × 10 <sup>-6</sup>                                  | 4 × 10 <sup>-4</sup>                                   |
| General population limit (GPL)                  | 1988                   | 3 × 10 <sup>-6</sup>                                   | 3 × 10 <sup>-6</sup>                                  | 1 × 10 <sup>-4</sup>                                   |
|   | 2003/2004              | 1 × 10 <sup>-6</sup>                                   | 6 × 10 <sup>-7</sup>                                  | 2 × 10 <sup>-5</sup>                                   |
| Immediately dangerous to life and health (IDLH) | 1988                   | N/A  | N/A   | N/A  |
|   | 2003/2004              | 1 × 10 <sup>-1</sup>                                   | 3 × 10 <sup>-3</sup>                                  | 7 × 10 <sup>-1</sup>                                   |
| Acute Exposure Guideline Levels <sup>a</sup>    |                        |  |   |  |
| 1-hr AEGL-1 <sup>a</sup>                        |                        | 2.8 × 10 <sup>-3</sup>                                 | 1.7 × 10 <sup>-4</sup>                                | 6.7 × 10 <sup>-2</sup>                                 |
| 1-hr AEGL-2 <sup>a</sup>                        |                        | 3.5 × 10 <sup>-2</sup>                                 | 2.9 × 10 <sup>-3</sup>                                | 1.0 × 10 <sup>-1</sup>                                 |
| 8-hr AEGL-1 <sup>a</sup>                        |                        | 1 × 10 <sup>-3</sup>                                   | 7.1 × 10 <sup>-5</sup>                                | 8.0 × 10 <sup>-3</sup>                                 |
| 8-hr AEGL-2 <sup>a</sup>                        |                        | 1.3 × 10 <sup>-2</sup>                                 | 1 × 10 <sup>-3</sup>                                  | 1.3 × 10 <sup>-2</sup>                                 |

<sup>a</sup>Acute exposure guideline levels (AELs) are a hazard communication measure developed by the National Advisory Committee to Establish Acute Exposure Guideline Levels for Hazardous Substances. The committee developed detailed guidelines for devising uniform, meaningful emergency response standards for the general public. The guidelines define three tiers of AELs as follows:

AEGL-1: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic nonsensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.

AEGL-2: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

AEGL-3: The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

NOTE: GA, tabun nerve agent; GB, sarin nerve agent; VX, nerve agent; HD, sulfur mustard (distilled).

SOURCE: Federal Register, 1988, 2003, 2004; NRC, 2003.

agent destruction operations until 2005, when the 2003/2004 values were implemented.

Following are two terms that warrant definition when discussing monitoring systems for NRT monitors:

- *Alarm level.* A predetermined value for an NRT method that, when equaled or exceeded, will result in an audible and/or visual alarm at the location of the NRT monitor. The alarm level must be set so that the statistical response rate at the alarm level is greater than or equal to 95 percent (U.S. Army, 2004a).
- *Action level.* A predetermined value, usually for an NRT method, that, when equaled or exceeded, indicates the need to conduct a series of required actions in response to the apparent detection of agent. An action level is typically less than the alarm level for an NRT monitor. Actions taken when the action level is exceeded (but the alarm level is not exceeded) may include checking to ensure that the NRT monitor is functioning properly, locating and correcting a leak

before the concentration of agent at the location being sampled exceeds the alarm level, and so on.<sup>3</sup>

### Specific Limit Definitions

In 2003 and 2004, the CDC published new recommendations for WPLs and GPLs for the nerve agents (Federal Register, 2003) and for sulfur mustard (Federal Register, 2004). The CDC also recommended values for two additional AELs—a short-term exposure limit (STEL) and an immediately dangerous to life and health (IDLH) concentration. The CDC determined that the GA and GB STEL exposures should be for no longer than 15 minutes (the same STEL exposure recommended for VX and HD), not to occur more than four times per day, and that at least 60 minutes

<sup>3</sup>Personal communication between Robert Durgin, chief, Monitoring Team, CMA; Jeff Kiley, Monitoring Office, Risk Management Directorate, CMA; and Gary Sides, committee member, on November 30, 2004.

should elapse between successive exposures. The STEL for VX was recommended to occur no more than one time per day. Exposure at the IDLH concentration can be for no longer than 30 minutes, the time in which an unprotected worker could escape without experiencing impaired or irreversible health effects.

Both old and new AELs are listed in Table 2-2. The new WPLs were reduced approximately threefold for the nerve agents and sulfur mustard, while the STELs were established at the old WPL levels. Thus, the 1988 WPLs and the 2003/2004 STELs are numerically identical for the respective agents. Although the CDC lowered the AELs in 2003/2004 by using updated and minimally modified risk assessment assumptions including consideration of uncertainties, it stated that the prior AELs have protected humans from the effects of these agents (Federal Register, 2003) (see Box 2-1). For more detail on the derivation of the new AELs and their comparisons to the 1988 AELs, see the NRC report *Impact of Revised Airborne Exposure Limits on Non-Stockpile Chemical Materiel Program Activities* (NRC, 2005).

The WPL is typically referred to as an 8-hour-per-day, 5-day-per-week exposure and is used as a time-weighted average (TWA) during the 8-hour exposure period. The Army, however, has been using the CDC WPL as a ceiling level rather than as a typical TWA, and it has consistently identified this AEL as a "TWA." Moreover, in the stockpile facilities, the Army has historically set the alarm level at 0.2 of the WPL. For example, the 1988 WPL for GB is  $1 \times 10^{-4}$  mg/m<sup>3</sup>, while the alarm was set to sound at 0.2 of this value ( $2 \times 10^{-5}$  mg/m<sup>3</sup>). The reason for using 0.2 of the WPL is to ensure protection within the 99 percent con-

fidence limit, taking into account the variation in the responses of analytical monitoring equipment to airborne agent concentrations.

The Army has accepted the new CDC AELs for the nerve agents and sulfur mustard, and it will use the STEL to set the alarm and action levels (U.S. Army, 2004a). Although the Army is recommending that the alarms in the stockpile facilities be set at the actual STEL, the environmental regulatory agencies in the states hosting demilitarization facilities have traditionally required that the alarms be set at a level less than the actual AEL. For instance, for GB, the states have required that the alarms be set at or near 0.2 of the AEL that comprises the current alarm level for GB. Thus, implementing the new AELs at 0.2 of the STEL has resulted in no changes in the monitoring alarm and action levels in the chemical demilitarization facilities. The Army plans to use the new WPL as an 8-hour-per-day, 5-day-per-week TWA. The Army's intent is to analyze monitoring data at the new WPL rather than at 0.2 of the WPL (U.S. Army, 2004b).

There are factors to consider in determining alarm and/or action levels. The current practice of setting the action levels at 0.2 of the WPL (Army TWA) has proven to be protective of worker populations (Federal Register, 2003). Thus, continuing with the same scenario (0.2 of STELs) seems to be practical. However, should a facility experience a large number of false alarms, the Army can encourage the states to seriously consider relaxing the 0.2 action level requirement. In fact, the Army has a permit from the state of Utah to use 0.5 of the STEL for VX at the Tooele demilitarization facility. The CDC developed the new AELs without recommending further reductions in the monitoring levels that the Army uses to protect the workers.

The new GPLs present additional problems because they are near the detection limit of the current historical monitoring system. The GPLs are based on continuous exposures for long periods of time that are unlikely to occur in the stockpile demilitarization operations. Army personnel have indicated that the public seems to be most interested in the Army being able to quickly identify a release that would be of concern to the surrounding general population. In order to satisfy that concern, the Army could consider area monitoring within the site and at the perimeter at much higher concentrations than at the GPL—that is, at a level of health concern that may require additional protective measures. For example, this alarm level within the site could be at or above the 1-hour AEGL-1 level (see Table 2-2), which would reduce false alarms and be indicative of a potential (above AEGL-1 level) health hazard for areas adjacent to the site. More detailed information concerning AEGLs can be found in the NRC reports, *Standing Operating Procedures for Developing Acute Exposure Guidelines Levels for Hazardous Chemicals* (NRC, 2001b), and *Acute Exposure Guideline Levels for Selected Airborne Chemicals: Volume 3* (NRC, 2003).

### BOX 2-1 Why Were the 1988 CDC AELs Changed?

The CDC reevaluated the 1988 AELs by using conventional reference concentration risk assessment methodology described by the U.S. EPA (Federal Register, 2003). It is recognized by the CDC that this method is conservative and the AELs are not numerically precise values to differentiate between nonharmful and dangerous conditions, nor are they precise thresholds of potential human toxicity. The CDC further states (Federal Register, 2003, p. 58350):

The recommended changes to the AELs do not reflect change in, nor a refined understanding of, demonstrated human toxicity of these substances but rather the changes resulted from updated and minimally modified risk assessment assumptions. Overt adverse health effects have not been noted in association with previously recommended exposure limits.

**Finding 2-1.** The Army's use of CDC's newly promulgated short-term exposure limits (STELs) as a basis for monitoring at demilitarization facilities is appropriate to ensure that workers are protected.

**Recommendation 2-1.** The committee recommends that the Army continue to use short-term exposure limits (STELs) as the basis for near-real-time monitoring.

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## 3

# Properties of Measurements and Measurement Systems for Airborne Agents

## MONITORING SYSTEM PROPERTIES

### Methods of Detection

Current monitoring systems used at stockpile disposal facilities to detect the presence of chemical agent in the ambient air and measure its concentration use an approach that involves air sampling. In this approach, the air being sampled is passed through a column containing an adsorbent for a certain period of time, after which the adsorbed molecules are thermally desorbed into a gas chromatograph (GC) equipped with an element-selective detector. The magnitude of the signal from the detector can usually be enhanced by increasing the volume of air passing through the adsorbent, resulting in the collection of additional agent. Selectivity is gained both by the GC separation and the use of an element-selective detector. This approach is discussed in detail in Chapter 4.

Other instruments that can be considered by the Army to measure the concentration of chemical agents in the ambient air are usually based on one of three principles: optical spectroscopy, mass spectrometry, or chemical sensing. These principles are briefly described below and are discussed in more detail in Chapter 5.

#### *Optical Spectroscopy*

All chemical agents absorb ultraviolet and infrared radiation at certain specific wavelengths. Most optically based instruments, such as Fourier transform infrared (FT-IR) spectrometers, measure the fraction of radiation absorbed by agents at one or more of these wavelengths, from which the concentration of the agent is calculated. Other optical techniques that have been proposed for monitoring chemical agents are based on the interaction of the agent molecules with a beam of monochromatic light. This interaction may involve inelastic scattering (Raman spectroscopy) or absorp-

tion of the light by the analyte followed by re-emission at a longer wavelength (fluorescence spectroscopy).

#### *Mass Spectrometry*

Mass spectrometric techniques involve ionizing the analyte by either soft ionization, in which the analyte molecules remain intact during the ionization process, or hard ionization, in which the analyte decomposes into ionized fragments. The ions that are formed are passed through a magnetic and/or electric field where they are separated on the basis of their mass-to-charge ratio ( $m/z$ ). When the separation is effected under a high vacuum, this technique is known as mass spectrometry. When the ions are separated by passing them through a gas at atmospheric pressure under a high electric field, the technique is known as ion mobility spectroscopy.

#### *Chemical Sensing*

Several new molecular-level chemical sensing systems that involve the binding of the chemical target species to a surface receptor to generate an electrical or optical signal are under development. Array-based sensors employing cross-reactive sensing materials have been used to identify chemical agents in a variety of background environments. New sensing materials with higher sensitivities and specificities for chemical agent detection are being developed; these include novel polymers and nanostructured materials. In addition, complete detection systems based on microfluidics and/or microelectromechanical systems (MEMS) have been developed for chemical agent detection.

#### **Open-Path and Point Monitoring**

As noted above, current practice at stockpile sites involves a two-step process to measure trace levels of

chemical agents in the ambient air. The analytes (along with many other molecules present in the air) are first collected on a suitable adsorbent by passing the sampled air through the adsorbent for a certain duration. At the end of this time period, the collected molecules are rapidly desorbed and passed into the instrument that is used for their detection and quantification (typically a GC equipped with an element-selective detector). Because the air that is sampled originates from one particular location, this approach is known as *point monitoring*. The equipment used for point monitoring may be permanently mounted at a specific location or mounted on a suitable vehicle so that sampling may be effected at different locations with a single instrument.

Point monitoring has the great advantage that the sample may be preconcentrated for a time, allowing the determination of agents at very low concentration. There are two main disadvantages of point monitoring techniques, however. First, the agent may be adsorbed on the tubing through which air is passed to reach the adsorbent; in this case, the reported concentration will be less than the true value. Second, the air that is being sampled may need to be passed through the adsorbent for several minutes or even hours in order to collect enough agent to give a detectable signal; thus, the concentration of the agent cannot be measured in real time (i.e., less than 10 seconds). If the time between successive measurements is less than 15 minutes, the measurement is said to be made in *near real time* (NRT). For measurements using current chemical agent monitoring technology at or near the general population limit (GPL), several hours are typically needed to preconcentrate the agent molecules to a detectable level. This approach is called *historical monitoring*.

The only way that the concentration of chemical agents can be monitored in real time (i.e., less than 10 seconds) is to eliminate the preconcentration step and to determine the molecule in situ. When this type of measurement is made by passing a light beam directly through the air that is being sampled, the technique is called *open-path monitoring*. The sensitivity of open-path measurements depends fundamentally on the product of the path length and the concentration of target molecules that are interrogated by the light beam. To maximize this number, the beam is usually passed through several hundred meters of the ambient air that is being sampled.

Open-path monitoring has two other potential benefits over point monitoring besides the enhanced capability for real-time measurement. First, the analyte is never lost by adsorption on the sampling surfaces in the preconcentration step. For this advantage to be realized in practice, the instrument must have high enough sensitivity that the analyte can be detected in the atmosphere at the desired concentration. The second advantage is that the light beam passes through several hundred meters of air; thus, the chance of an agent plume passing through the light beam is significantly greater than its passing through the location at which the point monitor is mounted. There is another significant difference

between point and open-path monitors in that point monitors using sample concentration techniques give the concentration of the agent averaged over the duration of the time that air is passed through the adsorbent, whereas open-path monitors give the average concentration of the agent in the light path (often called the path-integrated concentration) during the time it is interrogated.

## SENSITIVITY, SELECTIVITY, AND TIME RESPONSE TRADE-OFFS

### Limits of Detection and/or Quantification

The limit of detection for any analyte is the smallest quantity or concentration that can be detected to a certain confidence level (usually 95 percent). Two types of determinations should be distinguished: univariate (when only one analyte is measured by the particular sensor) and multivariate (when more than one analyte is determined). The chemical agent monitors currently used at stockpile disposal facilities rely on a univariate determination.

For a univariate determination, many textbooks on analytical chemistry give the limit of detection (LOD) as  $3\sigma$ , where  $\sigma$  is the standard deviation of the digitized signal from the detector (Ingle and Crouch, 1988; Christian, 2004). Assuming the baseline signal is randomly distributed about a mean value and 100 points are used to calculate  $\sigma$ , there is about a 1 percent probability that the maximum datum and the minimum datum will each be  $2.58\sigma$  from the mean in the absence of the analyte and any interferents. In practice, this consideration leads to the result that the LOD depends on the width of the signal relative to the frequency of the noise, since very narrow signals are more difficult to distinguish from noise than broader signals are, as shown in Figures 3-1A and 3-1B. A more stringent criterion for the LOD than  $3\sigma$  is probably called for to avoid false positives (see below). For example, Harris (1996) defines the detection limit of atomic spectrometry as the concentration required to give a signal that is three times the *peak-to-peak* noise level. Since the peak-to-peak noise level is about  $5\sigma$ , this criterion implies that the  $\text{LOD} = 15\sigma$ .

Similarly, the limit of quantification (LOQ) for a univariate analysis is usually given as  $10\sigma$ , which is approximately twice the peak-to-peak noise level. Again, a more stringent criterion should probably be applied if the analyte is to be determined to an accuracy of  $\pm 25$  percent at the true value with a 95 percent confidence level.

Open-path Fourier transform infrared (OP/FT-IR) spectroscopy (see Chapter 5) is an example of a multivariate analysis, since interferents will generally be present in the infrared beam at the same time as the analyte. In any multivariate analysis, a calibration step must be carried out with the analyte present along with all expected interferents. The result of this step is the calculation of the root-mean-square error of calibration (RMSEC). A completely independent

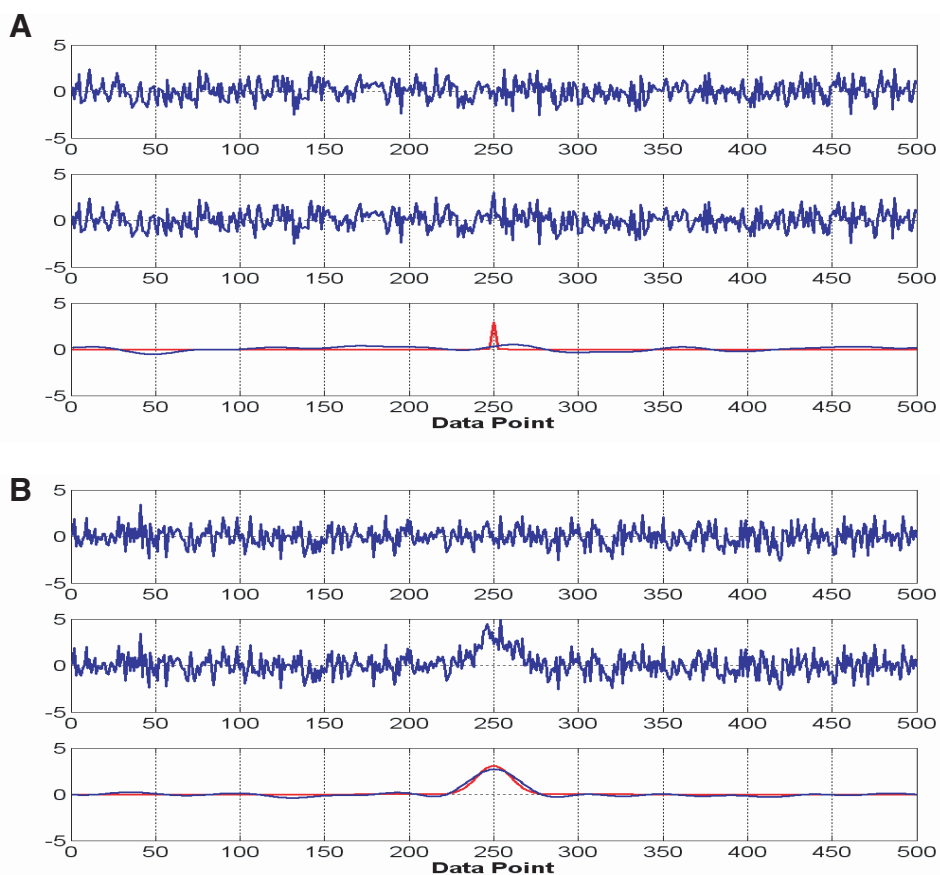


FIGURE 3-1 Random noise distribution using Gaussian peak. (A) (Top) Normally distributed random noise with a mean value of zero and a standard deviation of 1. (Middle) Same noise with a sharp Gaussian band (width of 1 and a height of 3); the peak cannot be observed visually despite the fact that its height is equal to  $3\sigma$ . (Bottom in red) The noise-free Gaussian peak that was added to the noise in the upper trace. (Bottom in blue) The result of smoothing the middle trace to remove the high-frequency noise; the peak cannot be observed. (B) Same data as in (A), but with the width of the Gaussian band equal to 10. In this case, the band can readily be seen above the noise level, especially after the smoothing function has been applied. SOURCE: Courtesy of Limin Shao, University of Idaho.

series of measurements is then taken to validate the calibration, which results in the calculation of the root-mean-square error of prediction (RMSEP), which may be considered to be equivalent to the standard deviation for a univariate analysis. In both the calibration and validation steps, the concentration of the analyte must be known. In the validation step, the concentration of the analyte in each sample is calculated from the calibration matrix and compared to the known concentration for this sample. The RMSEP is the standard deviation of the difference between the known and calculated concentrations of the analyte.

### Selectivity

In a univariate analysis, the predicted concentration could either be correct or it could be the result of an interferent that is present in the absence or presence of the analyte. For a

chromatographic determination, the closer that the retention time of the peak of interest is to the specified retention time of the authentic analyte, the greater the confidence that can be placed in the result. An interferent that elutes with a retention time approximately equal to that of the authentic analyte, and that gives rise to a signal at the GC detector, yields a false-positive result.

For any multivariate determination, the residual spectrum after the concentration of the analyte has been determined gives an indication of the presence of any other molecule(s) that was (were) not present in the calibration samples and hence the confidence that can be placed in the predicted concentration of the analyte. Obtaining or preparing a set of calibration data in which all possible interferents are represented is one of the larger challenges of multivariate methods of analysis such as OP/FT-IR spectroscopy.

### False Negatives and False Positives (Confirmation)

When the alarm level is close to the limit of detection, incorrect results may be indicated. *False negatives* occur when the target analyte is determined, through monitoring, to be present at a concentration below the alarm level but is in fact present at a concentration above the alarm level. Conversely, a determination in which the analyte is predicted to be present above the alarm level but is in fact absent, or present at a concentration below the alarm level, is known as a *false positive*. For the detection of chemical agents, false negatives mean that agent was present at a concentration greater than the alarm level, which is a potentially hazardous situation, whereas false positives may mean that the demilitarization process has to be shut down unnecessarily. Obviously, both situations are undesirable.

### Measurement Time and Measurement Trade-off

The time between the start of one measurement and the start of the next is the measurement time. When pre-concentration of a sample followed by a gas chromatographic separation is used, the measurement time is the sum of the duration for which air is passed through the adsorbent ( $t_A$ ), the time for thermal desorption of the adsorbates into the GC ( $t_B$ , usually short), the time to complete the elution of all the components from the GC ( $t_C$ ), and the data processing time ( $t_D$ , usually negligible). The time required for the thermal desorption, chromatography, and data processing ( $t_B + t_C + t_D$ ) is fixed. The amount of the analyte injected onto the GC column is directly proportional to the product of its average concentration, the flow rate of the air sample through the adsorbent, and  $t_A$ . To reduce  $t_A$ , the flow rate of air through the adsorbent could (in principle, at least) be increased. There is a trade-off, however: if the flow rate is too high, the efficiency of the adsorption is reduced so that there is a limiting flow rate above which the capture efficiency falls below 100 percent. In general, the lower the actual concentration of analyte in air, the greater the sampling time  $t_A$  required to achieve a significant signal-to-noise ratio. Thus, the signal-to-noise ratio of the measurement is directly proportional to  $t_A$ . The time required for a measurement of this type cannot be less than  $(t_B + t_C + t_D)$ . However, if a point sampling measurement technology is both sensitive enough not to require sample concentration ( $t_A = 0$ ) and specific enough not to require sample separation ( $t_C = 0$ ), then the measurement line ( $t_B + t_D$ ) can be very short, allowing real-time detection.

In an open-path measurement, the LOD depends fundamentally on the noise level on the spectroscopic baseline, which decreases with the square root of the data acquisition time. Thus, there is a smaller benefit to increasing the measurement time in an open-path measurement than in a point monitoring technique where the analyte is trapped on

an adsorbent. In an open-path measurement, a result may be obtainable in a few seconds. However, the uncertainty (LOD or LOQ) of this measurement is far worse than that obtained by a point monitoring technique and can only be improved by increasing the measurement time significantly. To obtain the same LOD as the point monitoring system described in the previous paragraph, the data acquisition time of an OP/FT-IR measurement is far greater than the total measurement time ( $t_A + t_B + t_C + t_D$ ).

### INTRODUCTION TO SAMPLING FOR GB, VX, AND HD IN AIR

An understanding of the key factors that impact monitoring for GB, VX, and HD at stockpile sites is a prerequisite to considering potential new air monitoring systems for use in the stockpile program or to suggesting upgrades to existing systems.

Airborne exposure limits (AELs) for the three agents of primary interest in the stockpile program are given in Table 2-2 in the preceding chapter. The concentration range from the GPL to the IDLH limit that must be measured for each agent is shown in Table 3-1. For a given AEL, existing Army quality assurance/quality control (QA/QC) monitoring guidelines given in the Chemical Materials Agency's *Programmatic Laboratory and Monitoring Quality Assurance Plan* require instruments to be calibrated between 0.5 AEL and 2.0 AEL (U.S. Army, 2004). Thus, for example, a given monitoring system (and its associated GPL method) must be capable of measuring VX GPL concentrations in the range of 0.000025 to 0.0001 ppb (0.0000003 mg/m<sup>3</sup> to 0.0000012 mg/m<sup>3</sup>).

Sampling methods must be capable of collecting agent at a given sampling station in periods of time ranging from a few minutes (for the confirmation of NRT alarms) to 8 to 12 hours (for historical monitoring). Also, NRT monitoring systems are required to sample and report within 15 minutes. Furthermore, monitoring systems must be relatively simple to operate and maintain and must operate continuously and reliably.

TABLE 3-1 Minimum and Maximum AEL Concentrations for VX, GB, and HD

| Agent | General Population Limit (GPL)             | Immediately Dangerous to Life and Health (IDLH) Limit |
|-------|--|---|
| VX    | 0.00005 ppb (0.0000006 mg/m <sup>3</sup> ) | 0.25 ppb (0.003 mg/m <sup>3</sup> )                   |
| GB    | 0.00017 ppb (0.000001 mg/m <sup>3</sup> )  | 17 ppb (0.1 mg/m <sup>3</sup> )                       |
| HD    | 0.003 ppb (0.00002 mg/m <sup>3</sup> )     | 99 ppb (0.7 mg/m <sup>3</sup> )                       |

NOTE: ppb = parts per billion by volume (1 molecule in 1 billion).  
 SOURCE: Federal Register, 2003, 2004.



Among factors to consider when sampling for chemical agents is that interaction of VX with a variety of surfaces (including Teflon<sup>®</sup> and glass) or hydrolysis of any agent may cause severe losses during sampling and analysis.

Another factor to consider when sampling for GB, VX, and HD is that the environments within and surrounding stockpile demilitarization facilities often contain other chemicals at concentrations as high as tens of parts per billion that may interfere with agent detection. Thus, interferent concentrations can be millions of times greater than the lowest concentrations at which the agents must be monitored. These chemicals include various natural and human-made hydrocarbons, organophosphorus-based pesticides, decontaminants (for example, bleach solution), agent reaction products, and products of the combustion of gasoline and diesel fuel. Because of the presence of these potential chemical interferents, the sampling-and-analytical systems used to monitor for GB, VX, and HD must exhibit selectivities approaching a million to one or better to minimize false positives. One other complicating factor is that the environments that must be sampled at stockpile disposal sites often contain dust and/or high humidity, and the temperature of the air being sampled may range from well below 0°F to approximately 100°F.

GB, VX, and HD are typically monitored using gas chromatographic systems containing heteroatom-specific detectors (see Chapter 4 for a detailed discussion of currently used monitoring systems). For example, both the conventional flame photometric detector (FPD) and the pulsed FPD (PFPD) are used for the detection of phosphorus in nerve agents in the form of HPO\* emissions, and for mustard agent, sulfur in the form of S<sub>2</sub>\* emissions (where \* implies that the species is in an excited state). In some instruments, the halogen-selective detector (XSD) is used for the detection of chlorine atoms in mustard agent. The limits of quantification for the FPD and the PFPD are typically at the picogram level for organophosphorus compounds and at the tens-of-picograms level for sulfur-containing (mustard) compounds. Thus, for the lowest AELs, it is usually necessary to collect agent from a minimum of several liters of air for analysis. The XSD is capable of the detection of picogram levels of HD. See Chapter 4 for further details concerning these detectors.

One other factor to consider is that it is difficult, if not impossible, to collect agents present in a given air sample without also collecting significant quantities of potential interferent compounds. Thus, it is desirable that any proposed sampling-and-analytical method include a means of separating the agents from the potential interferents collected prior to allowing the compounds to enter the detector. Also, the CMA's *Programmatic Laboratory and Monitoring Quality Assurance Plan* requires that the efficiency of recovery of agent from the sample medium and through the analytical path be in the range of 75 to 125 percent (U.S.

Army, 2004).<sup>1</sup> This requirement can only be met by using components that have inert or deactivated sampling-and-analytical paths to construct the sampling-and-analytical system, and by controlling the temperature of these components to prevent the loss of agents on surfaces within these components. Inert or deactivated surfaces also help reduce sample carryover from one measurement cycle to the next.

The *Programmatic Laboratory and Monitoring Quality Assurance Plan* also requires that each monitoring system be certified by passing a Class I precision-and-accuracy (P&A) study, which consists of the calibration of the monitoring system, followed by a series of challenges in the range from 0.5 to 2.0 AEL over a 4-day period. A linear regression of the found (reported) concentrations versus challenge (true) concentrations is then performed. The constants determined in the linear regression (slope and intercept) are then used to calculate the concentration for a true 1.00-AEL challenge. The reported concentration must be in the range of 0.75 to 1.25 AEL; that is, the reported recovery must be in the range of 75 to 125 percent. Also, at a true concentration of 1.00 AEL, the 95 percent confidence limits for the reported concentration must be within ±25 percent of the actual concentration.

Furthermore, for daily 1.00-AEL challenges during routine operation, NRT monitoring systems must yield found concentrations in the range 0.75 to 1.25 AEL 95 percent of the time. If this condition cannot be met, then the alarm level for the NRT system must be set so that 95 percent of all 1.00-AEL challenges result in an alarm and at least 75 percent of daily 1.00-AEL first challenges must yield found concentrations in the range of 0.75 AEL to 1.25 AEL. For manual monitoring systems, the reportable limit (action level) must be set so that 95 percent of daily 1.00-AEL challenges yield found concentrations greater than or equal to the reportable limit (U.S. Army, 2004).

## DATA PROCESSING (SIGNAL PROCESSING, DISPLAY)

Modern chemical sensing instruments employ computerized signal processing and data formatting algorithms to convert raw instrument signals into useful information that can be used to trigger alarms, confirm detection levels, or otherwise aid in efficient process management and operational safety. These automated signal and data processing activities are particularly important for real-time sensors, which are often based on optical or mass spectral sensing techniques. Such sensors are designed to provide high sensi-

<sup>1</sup>An "efficiency of recovery" above 100 percent does not mean that a higher concentration of agent was generated than was present, but instead is indicative of the precision and accuracy by which the analytical instrumentation is capable of determining the true measurement, as represented by 100 percent recovery.

tivity and specificity coupled with fast response times. These processing techniques entail measuring a signal that comprises a multitude of individual electronic measurement readings. The purpose of the processing module is to convert this multitude of measurements automatically into a visually (and/or audibly) recognizable detection indication, including an alarm when necessary, as well as to provide an electronic record of measurement results.

For example, in the metering of the temperature of a boiler, as depicted in Figure 3-2 (top), a single measured quantity is displayed on a gauge that can include an alarm trigger when the gauge needle exceeds some threshold value. A signal composed of a multitude of measurement readings, as represented by Figure 3-2 (bottom), presents a more diffi-

cult engineering challenge because the measured signal may exhibit complex patterns that defy simple means of automated detection and reporting. Instead, automated detection and reporting require the use of a computer chip running pattern-recognition software (algorithms). Fortunately, today's computing technology enables this to be readily accomplished by accommodating both a large number of measurements and enabling more computationally demanding, higher-performance algorithms to be applied in real time.

To illustrate how and why such pattern-recognition processing is applied, consider the example presented in Figure 3-3. Figure 3-3A shows a notional spectrum of a chemical agent, in pure form, at a low (safe) concentration. In an ideal world, the agent could be remotely measured in

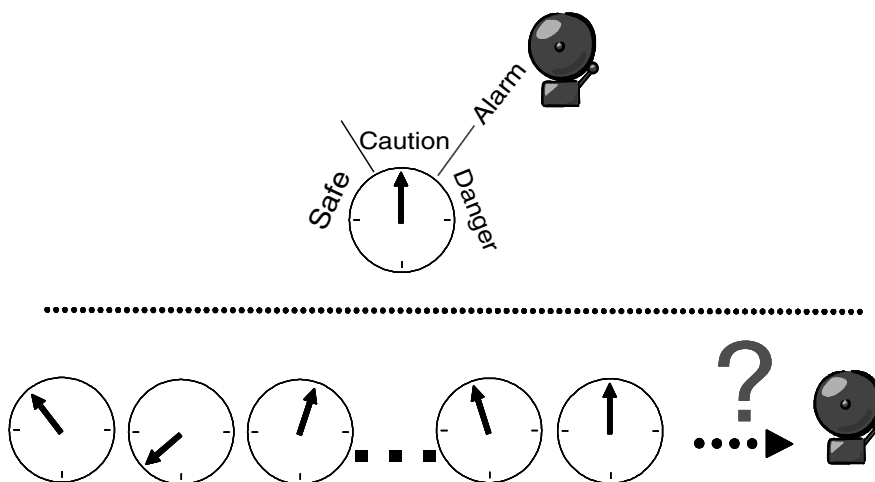


FIGURE 3-2 Illustration of simple and complex automated measurements. (Top) Simple automated detection and reporting of a simple measurement—boiler temperature; (bottom) a multitude of measurement readings, exhibiting complex patterns, defies simple means of automated detection and reporting. SOURCE: Courtesy of Frank Iannarilli, Aerodyne Research, Inc.

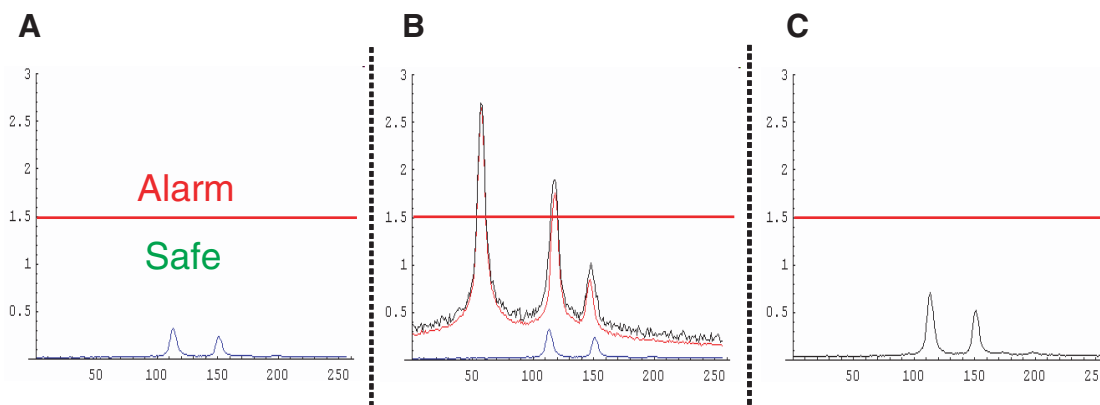


FIGURE 3-3 Depiction of pattern recognition applied to spectral detection of chemical agent. (A) Spectrum of pure agent at low concentration; (B) spectral measurement (black curve) showing the additive composite of low-concentration agent (blue curve) in a strongly interfering background (red curve); (C) result of pattern-recognition algorithm on (B), digitally suppressing much of the interfering background, and correctly indicating a safe agent concentration level. SOURCE: Courtesy of Frank Iannarilli, Aerodyne Research, Inc.

pure form, and one could automatically detect dangerous concentrations by the alarm's sounding when the agent's spectral peak readings exceeded the depicted alarm threshold. This might be implemented with simple electronic wiring.

Figure 3-3B depicts the chemical agent, still at the same safe concentration, but now as measured in the real world, which adds a strongly interfering background. This background exhibits three spectral peaks, all above the alarm threshold, including two at the locations of the chemical agent's characteristic spectral peaks. Surely, no one individual or small set of readings within this spectrum, which comprises 250 measurements, is sufficiently informative for reliable automated detection.

Figure 3-3C shows the result of a simple pattern-recognition algorithm upon processing the real-world measurement in Figure 3-3B. By making use of the known spectral pattern of the chemical agent in pure form (Figure 3-3A), this algorithm is able to digitally suppress<sup>2</sup> much of the background interference exhibited in the real-world measurement (Figure 3-3B). The result correctly indicates a low concentration of chemical agent, somewhat in excess of the true concentrations, but still well below the alarm threshold.

A certain level of reliability from an automated detection, processing, and reporting module is necessary. There are numerous ways of quantifying such reliability, such as the likelihood of detecting a chemical release (of given concentration) versus the frequency of false alarms. There exists a well-established body of knowledge for determining the achievable reliability of such automated pattern-recognition schemes, both as a function of cost/complexity and their intrinsic physical limits. Further discussion of modern signal detection and processing techniques are available in Duda et al. (2001), Hastie et al. (2001), and Scharf (1991).

## RELIABILITY AND MAINTAINABILITY

Any time that a monitoring system is not completely functional at a chemical stockpile disposal facility, the potential exists for erroneous decision making and hence for either missing a true event or closing the plant on a false alarm. Reliability is the measure for the fraction of times that monitoring instruments pass tests of their continued ability to perform correctly. Instruments can fail in two ways. First, they can fail because they are not working (e.g., they may be broken or disconnected). Second, they can fail to give a correct result. The latter form of failure is covered in the

<sup>2</sup>The algorithmic procedure is to (1) subtract the spectrum's average measured value from each of the spectral measurement samples; (2) multiply each spectral measurement, point-by-point, with its corresponding spectrum value for the pure chemical agent; (3) sum the resulting multiplicative product terms to arrive at a scale factor value; and (4) finally, apply this scale factor to the spectral "template" pattern of the pure chemical agent, and add in a mean bias term.

next section, in which the complete human/instrument system is considered from the point of view of avoiding false negatives and false positives; this section concentrates on the former failure mode.

All of the instruments used in chemical demilitarization monitoring have good reliability in terms of the fraction of tests passed. However, with such a large number of instruments, the overall failure of the system is caused by failure of any one of the instruments, meaning that the system fails more often than its components do. For example, if each of 100 instruments only malfunctions once per year, then the probability of a system failure caused by any instrument failure is 0.24 per day, meaning that the system fails approximately 1 day in 4.<sup>3</sup> This would probably not be acceptable to the public. Increasing system reliability involves the following:

- Using highly reliable instruments and people—that is, mean time between failures must be as low as possible for both. This implies highly reliable instruments, which appears to be the case, and highly reliable operators, which means constant training and reinforcement of correct operating procedures.
- Building reliable systems even if components are inherently unreliable, using planned redundancy, and so on.
- Reducing mean time to repair using design for maintainability and similar approaches. Current NRT agent monitors are designed to be tested and then replaced for off-line repair if they do not pass each functional test. Observations of the testing procedure and reading of its manual suggest that the test system is rapid and, if procedures are followed, reliable. No attempts have been made to quantify the maintainability of the instruments, for example using the Bretby Maintainability Index (Rushworth and Mason, 1992).

Good design uses all three of the above approaches together to achieve greater system reliability.

## OPERATOR AND OPERATING SYSTEMS INTERFACES

At stockpile sites, the output from any monitoring system is ultimately passed to a human operator for a final decision. The monitoring equipment and the operator together form a detection-and-decision system. The operator's task is to make the correct decisions based on the best available data, where "correct" means a decision that the decision-system administrators and the public would have wanted the operator to make in perfect hindsight. In monitoring, the

<sup>3</sup>This assumes 100 independent instruments, each with a failure rate of  $1/365 = 0.00275$  per day. Probability (p) (at least one instrument fails)  $= 1 - (1 - 0.00275)^{100}$ .

detection systems may have differing sensitivity settings, resulting in different reactivity and reliability. The “operators” can be the personnel directly working with a system—for example, the technician who has just brought a system back online or a remote operator in the main control room. Their decision results in an action, either putting the system into a safe condition or allowing it to continue operating.

From signal detection theory, which is a well-documented performance theory for making decisions under uncertainty, two factors affect the decision made by any human operator on the basis of data received from the monitoring instrument. The factors are:

- Discriminability of signal from noise, and
- Bias affecting the choice of criterion for reporting the signal.

Discriminability is a measure of the absolute difficulty of the decision task, that is, how easy or difficult it is to reliably determine the difference between signal and noise. Here the signal is defined as a true alarm, that is, a concentration that exceeds the amount needed to cause an action response to be taken. The noise is the statistical background fluctuation of the output from the system against which the signal must be detected. It can include random background noise, monitoring equipment noise, or the presence of interferents.

The threshold for reporting signal or noise depends on the criterion chosen by the operator. When the system output exceeds the criterion, the operator response is “signal”; otherwise the response is “no signal,” which is usually no response at all—that is, continue operations. The choice of criterion is affected by the prior probability of an event being a signal and by the costs and rewards for the different outcomes. The lower the a priori probability of a signal, the more the criterion will move toward not calling it a signal. “Costs and rewards” are not typically monetary, but rather represent the instructions as interpreted by the operator. This is not necessarily the same as the formal policy of written instructions unless those instructions are consistently applied. For example, if supervisors and colleagues reward productive behavior that is not strictly in accordance with policy, then the implied policy affects the criterion rather than the official policy.

In chemical demilitarization activities, many decisions have a high cost associated with them. Failing to put the system into a safe state when a signal occurs (a true positive) can endanger plant personnel and the public. Conversely, reacting when there was in fact no true event (false positive) is extremely costly in terms of processing time lost before the plant returns to normal operating conditions. Human decision makers do not always react correctly when the stakes are high and one event (a hazardous event) is inherently unlikely. Moreover, there are other general human factors problems for operators at chemical stockpile sites. First, difficult decisions that must be made rapidly under

uncertain conditions are stressful to some operators. Stress, particularly time stress, can affect decision making as people seek easily available solutions, for example, solutions that have worked under similar conditions in the past. Such “recognition primed decision making” (Klein, 1989) usually works well, but it can give the wrong answer if the operator “recognizes” conditions that do not apply in this instance. Another source of operator problems is complacency, defined technically as excessive trust in automated systems (Lee and Moray, 1994). This is the opposite of operators’ distrust of an instrument reading, but both represent an inappropriate level of trust in the monitoring system.

The problems described above are compounded by the operators’ knowledge that the monitoring instruments are operating at close to their technical limits. Human factors engineering can aid systems design by applying formal models, such as signal detection theory, and by using other models, such as interface design models, to improve the reliability of the decision maker.

Discriminability can be improved by ensuring that the interface to the operator is well designed. This interface consists of the physical interface of the equipment—for example, the controls and displays on the equipment—and the interface through the computer system that provides the monitoring information remotely. The interface also includes any person-to-person interaction between the operator who interfaces with the physical system and the person who makes the ultimate decision. Any documentation, such as the plans and policies promulgated by the Army to control operations, is part of the interface. Finally, the information from the interface is interpreted by the operators in terms of their knowledge and training. Training and practice have a large impact on how reliably the monitoring instruments are interpreted.

Interface design for the monitoring system should follow models of human factors good practice—for example, compatible control-display relationships or design for human-computer interaction. More modern models for interface design include ecological interface design that makes the interface compatible with the operator’s underlying models of the process. Any changes to the design must recognize that the current operators have long experience with the existing system. They have developed skills in operating and maintaining the equipment, so new designs must not contradict these learned skills but rather complement them in the new context. It is much more difficult for a human to learn a skill that conflicts with an already-learned skill than to learn a new skill unrelated to the older one.

Training of operators is particularly important when they must monitor automated equipment for rare events. As true events are extremely rare but false-positive alarms are an almost daily occurrence, the operator’s rational decision is to assume that any new alarm is also false (Wickens and Hollands, 2000). This is, of course, the wrong decision, but in an earlier NRC report on chemical events at chemical



agent disposal facilities (NRC, 2002), such behavior was found in most of the true events. False positives affect operators by “crying wolf” and make it more difficult for operators to maintain the mind-set of “true until proven false.” As a true event requires additional actions, from sending a person in a mask to investigate through to shutting down the plant, operators may be even more reluctant to treat all alarms as true events. The only way to alleviate the problem is by constant training and drills, including the use of unannounced false positives being inserted into the system specifically for training purposes.

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## 4

# Current Chemical Agent Monitoring Systems

### OVERVIEW OF CURRENT AIR MONITORING SYSTEMS

The monitoring systems currently used for the detection of the airborne agents GB, VX, and HD at fixed sampling locations at stockpile disposal sites and at agent storage facilities are these:

- ACAMS (Automatic Continuous Air Monitoring System),
- MINICAMS® (Miniature Chemical Agent Monitoring System), and
- DAAMS (Depot Area Air Monitoring System).

ACAMS and MINICAMS are automated near-real-time (NRT) monitoring systems that have been used in chemical agent disposal facilities since 1990 to monitor for these three agents at the Centers for Disease Control and Prevention's (CDC's) 1988 time-weighted average (TWA) airborne exposure limits (AELs) and at AELs that are immediately dangerous to life and health (IDLH) for GB and VX; the IDLH AELs were defined at a later date.<sup>1</sup> As described in Chapter 2, the Army has replaced use of the 1988 TWA AELs for agent monitoring with new, short-term exposure limit (STEL) AELs that were promulgated by the CDC in 2003 for nerve agents and 2004 for mustard agent. ACAMS and MINICAMS continue to be used for NRT monitoring at the new AELs. DAAMS, a manual monitoring system, has been used at stockpile and storage sites primarily to confirm the detection of 1988 TWA levels of agents by ACAMS or MINICAMS and to conduct historical monitoring at the 1988

TWA and general population limit (GPL) levels. DAAMS continues to be used in this manner at the new 2003/2004 AEL levels. ACAMS and MINICAMS have also been used to monitor airborne concentrations of agents at the limit-of-use concentration of 100 mg/m<sup>3</sup> for the totally encapsulated demilitarization protective ensemble (DPE) suits that workers use at chemical demilitarization sites (U.S. Army, 2004b).

Several different configurations of Agilent-gas-chromatograph-based, automated NRT monitoring systems have also been used or tested at various storage and disposal sites. These systems are known by the acronym A/DAM (Agilent/Dynatherm agent monitor). The latest version of the A/DAM system consists of a Dynatherm IACEM 980 sorbent-based sampling system connected to an Agilent 6852 gas chromatograph (GC).

In addition to fixed-site monitoring, ACAMS, MINICAMS, and the A/DAM system have also been used in mobile applications. In these applications, the NRT monitors and associated support systems are mounted in mobile vans, which are then driven to remote sampling locations (such as storage igloos) to conduct air monitoring.

The operation and performance of the MINICAMS, A/DAM, and DAAMS monitors were described in a recent National Research Council report (NRC, 2005) on air monitoring for the non-stockpile program. In the present report, the committee summarizes from the previous report only the information most relevant to this study, adding information regarding the ACAMS and its performance.

### Description of the ACAMS and MINICAMS

The ACAMS is being used at four incinerator-based stockpile disposal sites in the continental United States, and it had been used at the now-closed Johnston Atoll site in the Pacific Ocean southwest of Hawaii. The MINICAMS is currently in use at two sites that destroy agents by chemical neutralization. Both of these monitors provide reports of air-

<sup>1</sup>The 1988 CDC TWA AELs were defined in the Federal Register as "control limits for chemical agents," which were stated as specific numerical concentrations with an "averaging time" of 8 hours (Federal Register, 1988). As of 1988, the U.S. Army's stockpile disposal program had been using the same numerical values and referring to them as 8-hour time-weighted averages, or TWA values, since about 1978. IDLH AELs for GB and VX have been used by the Army since the 1990s (U.S. Army, 1997).

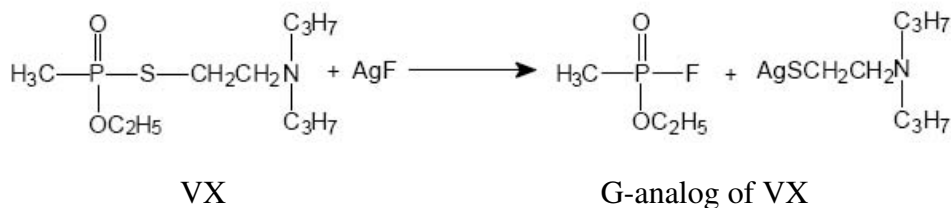


FIGURE 4-1 Derivatization of VX.

borne agent concentrations once every 3 to 15 minutes (U.S. Army, 2003). ACAMS and MINICAMS monitors used at stockpile sites are typically configured for sampling using glass tubes packed with a porous polymer. Separation of agents from potential chemical interferences is accomplished using temperature-programmed capillary gas chromatography. ACAMS monitors are configured for the detection of GB, VX, and HD using a flame photometric detector (FPD). MINICAMS monitors are typically configured with an FPD for the detection of GB, VX, and HD, or with a halogen-selective detector (XSD) for the detection of HD.

#### Principles of Operation

GB and HD are sampled and detected directly by ACAMS and MINICAMS monitors. However, because VX has low volatility and high affinity for irreversible adsorption on surfaces, it is first derivatized, as shown in Figure 4-1, by reaction with silver fluoride to yield the more volatile and less reactive G-analog of VX, which is then sampled and detected by ACAMS and MINICAMS monitors.

The derivatization of VX is accomplished in real time by installing a V-to-G conversion pad on the inlet of the NRT monitor or on the distal end of a heated sample line connected to the inlet. The conversion pad consists of a porous, polyester-felt pad impregnated with potassium fluoride and silver nitrate.

#### Detection Interferences

The FPD may be operated in a phosphorus-specific mode (by monitoring  $\text{HPO}^{*2}$  emissions through a 525 nm, narrow-band-pass optical filter) or in a sulfur-specific mode (by monitoring  $\text{S}_2^*$  emissions through a 396 nm, narrow-band-pass optical filter). In the phosphorus-specific mode, the FPD is about 10,000 times more sensitive to phosphorus than to carbon on the basis of signal per unit of mass for the range of interest when monitoring at STEL levels for GB and VX—about 1 to 10,000 picograms (pg) per second of phosphorus into the detector). In the sulfur-specific mode, the FPD is also about 10,000 times more sensitive to sulfur than to

carbon for the mass range of interest when monitoring for HD at STEL levels—about 100 to 100,000 pg per second of sulfur into the detector<sup>3</sup> (Thurbide and Aue, 1994). The FPD is less selective for phosphorus versus sulfur than for phosphorus versus carbon. Thus, despite the selectivity of the FPD, sulfur emissions (resulting from the formation of  $\text{S}_2^*$  in the FPD) as well as hydrocarbon emissions (for example, resulting from the formation of  $\text{CH}^*$ ) can cause interferences (false positives) in the phosphorus-specific mode. Also, phosphorus-containing compounds that are not agents but have the same GC-column retention time as GB or the G-analog of VX, and phosphorus-containing compounds other than VX—for example, certain pesticides—that also undergo V-to-G-analog conversion can cause false positives in the phosphorus-specific mode. In addition, hydrocarbons can quench (reduce) sulfur and phosphorus emissions, causing false negatives. For example, a concentration of only a few parts per million of a hydrocarbon, present in an area sampled by MINICAMS and with the same retention time as the agent being monitored, can result in the reduction of phosphorus or sulfur emissions by about 50 percent (Aue and Sun, 1993).

The XSD used in some MINICAMS to detect the chlorine in HD is a thermionic device based on work patented by Rice (1951) and Roberts (1957) and produced commercially by O-I Analytical. The target analyte is oxidized in a flame to produce halogen atoms that react with an alkali-activated, negatively biased platinum electrode enhancing its electron emission. In HD demilitarization facilities, potential interferences containing Cl are apparently much less abundant than those containing S, so MINICAMS utilizing XSD detectors are much less likely to produce false-positive detection than those using FPDs.

#### Calibration, Certification, and Quality Assurance

Before use, each NRT monitor must be calibrated. Calibration consists of injecting known masses of agent into the inlet of the monitor during successive instrument cycles—

<sup>2</sup>The asterisk symbol as used here indicates an excited electronic state.

<sup>3</sup>Note: Because sulfur emissions observed with the FPD are quadratic and hydrocarbon emissions are linear, the selectivity of the FPD in the sulfur-specific mode (with respect to hydrocarbons) is not constant but instead depends on the mass flow rate of sulfur into the detector.

specifically, microliter volumes of a dilute solution of agent are injected. Thus, the response (detector signal) versus the mass of agent can be determined.

After calibration, the responses obtained during subsequent cycles of operation of the NRT monitor can be converted to detected masses and to concentration readings, which are then reported as found concentrations, that is, agent concentration readings reported by the NRT monitor.

Monitoring systems (and their associated written methods) used at stockpile disposal sites must be certified before use in accordance with requirements stated in the Chemical Materials Agency's (CMA's) *Programmatic Laboratory and Monitoring Quality Assurance Plan* (U.S. Army, 2004a). Certification generally includes passing a 4-day precision-and-accuracy (P&A) study. P&A studies are usually conducted over a relatively narrow concentration range, typically 0.2 to 1.5 AEL in the past and now 0.5 to 2.0 AEL (as presented in U.S. Army, 2004a). The goals of a P&A study are (1) to demonstrate that when used for the detection of a true agent concentration of 1.00 AEL, the monitoring system (and its associated written method) is predicted to report a found concentration in the range of 0.75 to 1.25 AEL (that is, 75 to 125 percent recovery)<sup>4</sup> with a precision of  $\pm 25$  percent with 95 percent confidence, and (2) to document the P&A of the monitoring system at all concentrations used in the study (U.S. Army, 2001).

Monitoring systems and written methods are generally not tested formally outside the concentration range required for the P&A study (U.S. Army, 2004a). Thus, the accuracy of a given monitoring system for concentrations outside the range tested is generally considered to be uncertified. This fact is important to keep in mind when using the performance of monitoring systems and methods at the 1988 CDC 0.20 to 1.50 AEL concentration ranges to predict the expected performance at the 2003/2004 CDC 0.50 to 2.00 AEL concentration ranges.

### Description of the A/DAM System

As noted previously, several different configurations of the A/DAM system (which consists of an Agilent GC connected to a Dynatherm thermal desorption unit) have been used or tested at various storage and disposal sites. A/DAM systems are typically configured for sampling using glass tubes packed with a porous polymer. Separation is accomplished using temperature-programmed capillary GC, and detection is done via an FPD. The A/DAM system can be configured to achieve better chromatographic resolution (and

thus better selectivity) than can be achieved by ACAMS and MINICAMS monitors and, therefore, may experience fewer false positives.

The A/DAM system can also be configured with two separate GC columns and with two separate FPDs. In this configuration, gas streams exiting the Dynatherm thermal desorption unit can be split between the two analytical channels. If the two columns have liquid phases that are sufficiently dissimilar (for example, nonpolar and polar), a given agent will be detected at two different retention times on the two different analytical channels. Other potential interferences (for example, hydrocarbons) are unlikely to exhibit the same retention times as those for the agent on the two different columns. In this manner, a much higher degree of selectivity than that of the ACAMS and MINICAMS monitors is possible.

Agilent is introducing enhancements to the FPD to obtain a twofold to fivefold improvement in the signal-to-noise ratio.<sup>5</sup> Work has also been done on a method for the direct detection of VX that, for some monitoring applications, may allow the determination of VX without the need for derivatization, and thereby may result in fewer false positives than for the detection of VX using the V-to-G-analog conversion method (NRC, 2005).

Although A/DAM systems have been proven capable of monitoring at the CDC's 1988 TWA levels for GB, HD, and VX at several sites during the past 10 years, there are significant barriers to the widespread use of these systems. These barriers include greater cost, size, weight, and complexity compared with ACAMS and MINICAMS monitors. However, the greater analytical flexibility of the A/DAM system compared with ACAMS and MINICAMS monitors may reduce the importance of these barriers in the future, especially when monitoring sites or operations for which numerous false positives have been experienced when using ACAMS or MINICAMS monitors.

### Description of the DAAMS

The concentration of agent is currently determined by DAAMS to provide historical monitoring data at the worker population limit (WPL) and the GPL AELs. DAAMS samples are also analyzed to confirm or deny alarms sounded by NRT monitoring systems. Manual DAAMS samples are collected by pulling air through glass sampling tubes packed with a porous polymer for periods of time ranging from a few minutes for NRT confirmation samples to as long as 12 hours for GPL historical monitoring. Sampling tubes are placed at various locations within a given site. Most of the

<sup>4</sup>The phrase "75 to 125 percent recovery" means that the predicted signal for a true agent concentration of 1.00 AEL must be within 75 to 125 percent of the average signal obtained for a true concentration of 1.00 AEL (when the instrument is calibrated using only 1.00-AEL challenges).

<sup>5</sup>Letter from Wayne Abrams, senior consultant, Agilent Technologies, to John Decker, CDC National Center for Environmental Health, May 31, 2002.



sampling tubes for WPL AELs are co-located with NRT monitors (ACAMS or MINICAMS).

The analysis of DAAMS samples is usually accomplished using an Agilent Model 6890 or Model 6852 GC connected to a Dynatherm ACEM 900 or to a Dynatherm IACEM 980 thermal desorption system, which is configured to receive and desorb manually collected samples. For samples collected and analyzed in support of historical monitoring, the DAAMS GC is usually configured with an FPD. DAAMS GCs used to confirm or deny NRT monitoring alarms may also be configured with either an electron impact (EI) or chemical ionization (CI) mass selective detector (MSD), or with both an FPD and an MSD.

Because the analysis of DAAMS samples is based on the use of laboratory-grade GCs, which may be configured in many different ways, the configuration of DAAMS GCs varies from site to site. Most DAAMS GC systems in use at stockpile sites include a precolumn and an analytical column in series. In this configuration, low-boiling compounds and agents are first allowed to pass from the precolumn into the analytical column. The flow of carrier gas within the precolumn is then reversed to allow high-boiling compounds to be backflushed from the precolumn to clean and ready it for the next sample to be analyzed. While the precolumn is being backflushed, carrier gas continues to flow through the analytical column and into the detector, allowing the detection of the agents of interest.

The initial step in the analysis of a DAAMS sample consists of inserting the sampling tube into a port on the Dynatherm thermal desorption unit. Agent desorbed from the sampling tube is first collected on a sorbent bed in a small-bore focusing tube within the Dynatherm unit. Agent is then desorbed from the small-bore tube into the precolumn within a narrow band. For this reason, the DAAMS typically achieves better chromatographic resolution than do ACAMS or MINICAMS monitors and thus is more selective and experiences fewer false positives (interferences) than do the NRT monitoring systems. This often enables DAAMS monitors employing FPD detectors to be used effectively to confirm or deny the presence of agent in areas monitored by ACAMS or MINICAMS monitors. However, since DAAMS analyzers with FPD detectors do use the same basic agent detection scheme as FPD-equipped ACAMS or MINICAMS, they are often subject to the same measurement interferences and errors. DAAMS equipped with EI and/or CI MSDs employ an independent detection method that can be very useful in both identifying and discriminating against interferences.

### Performance of ACAMS, MINICAMS, and DAAMS Monitors

The current ACAMS, MINICAMS, and DAAMS concentration ranges shown in Figures 4-2 through 4-4 reflect the performance of these systems when monitoring at the CDC's 1988 AELs, performance proven at several different

stockpile sites during the past 10 to 15 years.<sup>6</sup> The CDC's 2003/2004 AELs and 1988/1997 required operating ranges for GB, VX, and HD are also presented in Figures 4-2 through 4-4.<sup>7</sup>

As noted previously, VX is detected as its G-analog, which differs from GB only by the presence of an ethyl group in place of an isopropyl group (in Chapter 2, see the section entitled "Chemical Agent Properties" for GB structure). Thus, it is likely that ACAMS and MINICAMS monitors could be successfully certified for GB at concentrations at least an order of magnitude less than the lower limit shown for the 1988/1997 ACAMS/MINICAMS range in Figure 4-2. (This extension of the GB lower detection limit vis-à-vis the 1988/1997 ACAMS/MINICAMS range for VX is shown by the dotted line to the left of the 1988/1997 ACAMS/MINICAMS line at the top of Figure 4-2.)

Previous NRC reports have expressed concerns about the frequency of false alarms experienced by ACAMS (NRC, 1994, 1999, 2002). During the past few years, the CMA and various sites have initiated or completed several actions in efforts to reduce the frequency of false alarms at stockpile disposal sites. For example, during the past few years, more than 700 chemicals and other chemical-source items have been tested at the Tooele Chemical Agent Disposal Facility (TOCDF) to identify whether they interfere with the operation of ACAMS monitors (that is, to determine whether vapors from these sources resulted in a positive response from ACAMS monitors). Chemicals or chemical-source items that are proven to be or that produce interferences are then banned from the site, or, if no suitable substitute can be found, the on-site use of these chemicals or chemical sources is carefully controlled.

This committee recently received a breakdown of ACAMS false-positive alarms (with the alarm level set at 0.50 of the 1988 TWA) during several months of VX disposal operations in 2003 and 2004 at TOCDF (Tooele, Utah). This information is shown in Table 4-1.

The false-alarm rates listed are the total number of ACAMS cycles that resulted in alarms (that is, concentration readings greater than 0.50 of the 1988 TWA, which is equal to the current STEL) and that were proven false by the analysis of co-located DAAMS samples. The average number of cycles that resulted in VX false alarms for the periods listed was 36 cycles per month out of nearly 1 million ACAMS

<sup>6</sup>An assessment of the routine performance of the A/DAM system by the committee was not attempted, because this system has been used only sparingly to date at stockpile storage and disposal sites, has been fielded in several different configurations, and has been used primarily for intermittent monitoring in mobile applications (as opposed to continuous fixed-site monitoring, which has been conducted almost exclusively using ACAMS, MINICAMS, and DAAMS monitors).

<sup>7</sup>The years 1988, 2003, and 2004 refer to years in which the CDC published AELs for GB, VX, and HD; the year 1997 refers to a year in which the Army published IDLH levels for GB and VX.

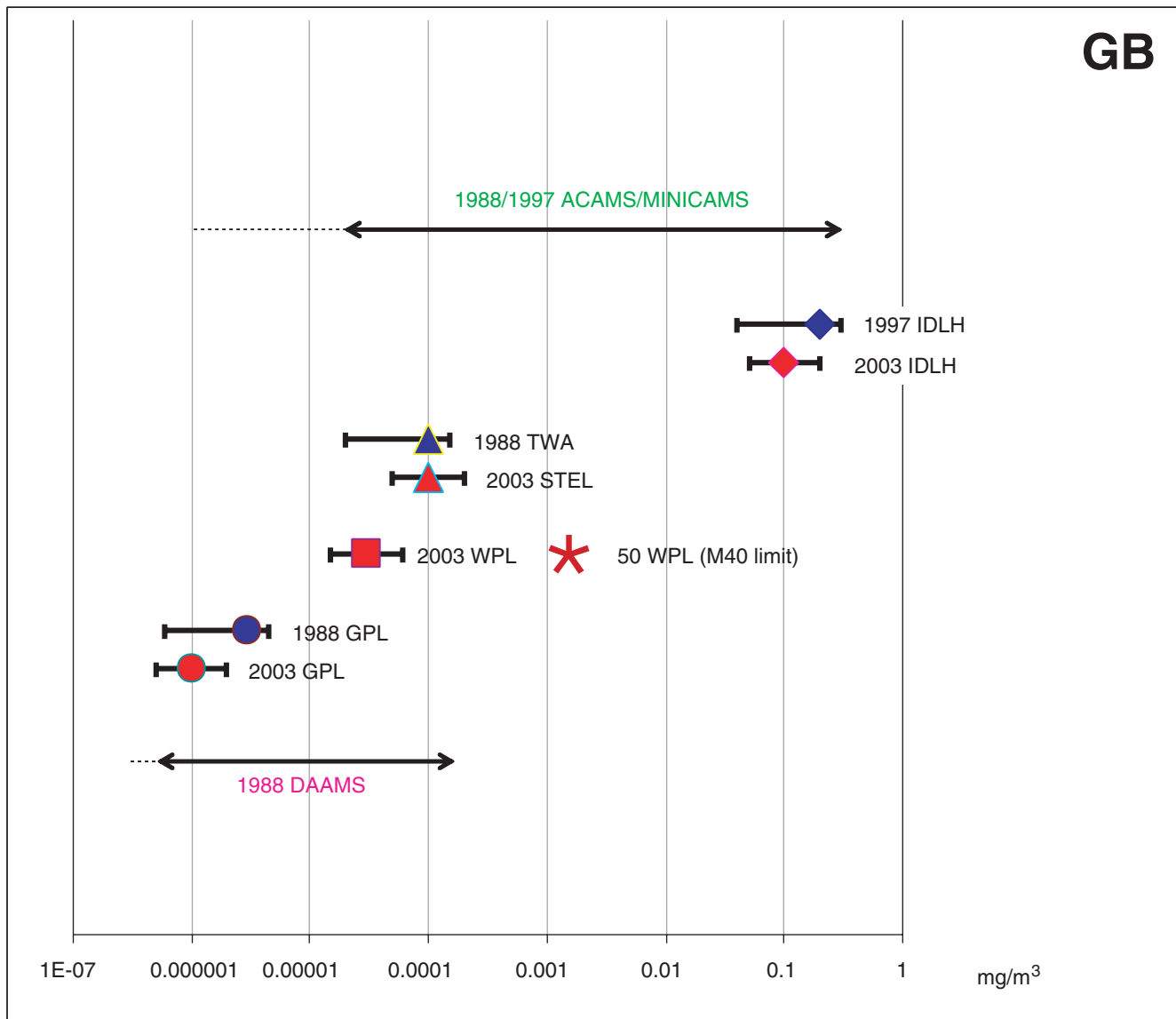


FIGURE 4-2 ACAMS/MINICAMS and DAAMS operating ranges for the 1988/1997 GB AELs and required ranges for the CDC's 2003 GB AELs.

NOTES:

(1) The 1988/1997 AEL concentration ranges for GB over which MINICAMS and DAAMS have been certified and operated for many years are indicated by horizontal lines that end in arrows. Also represented are the following:

- The "1988/1997 ACAMS/MINICAMS" line includes a dotted line to its left to indicate that it should be possible to calibrate and certify MINICAMS for monitoring GB at phosphorus-equivalent concentrations corresponding to 0.20 to 1.50 TWA of VX.
- The "1988 DAAMS" line also has a dotted line to its left to indicate that it should be possible to calibrate and certify DAAMS for monitoring GB at phosphorus-equivalent concentrations corresponding to 0.20 to 1.50 of the 1988 GPL for VX.
- The IDLH AELs are indicated by diamonds with range bars showing the past concentration range for certifying MINICAMS, 0.20 to 1.50 of the 1997 IDHL value for GB, and the concentration range required in the future, 0.50 to 2.00 of the 2003 IDHL value for GB.
- The CDC's 1988 TWA AEL and the numerically equivalent CDC's 2003 15-minute STEL for GB are indicated by triangles with range bars.
- The CDC's 2003 WPL for GB is indicated by a square with range bars, and the 1988 and 2003 GPLs are indicated by circles with range bars.

(2) The GB concentration limit above which negative-pressure respirators, such as the M40 mask, may not be worn is marked by an asterisk and labeled "50 WPL (M40 limit)." Limits for supplied-air respirators (1,000 WPL) and SCBA (10,000 WPL) are not shown.

SOURCE: NRC, 2005.

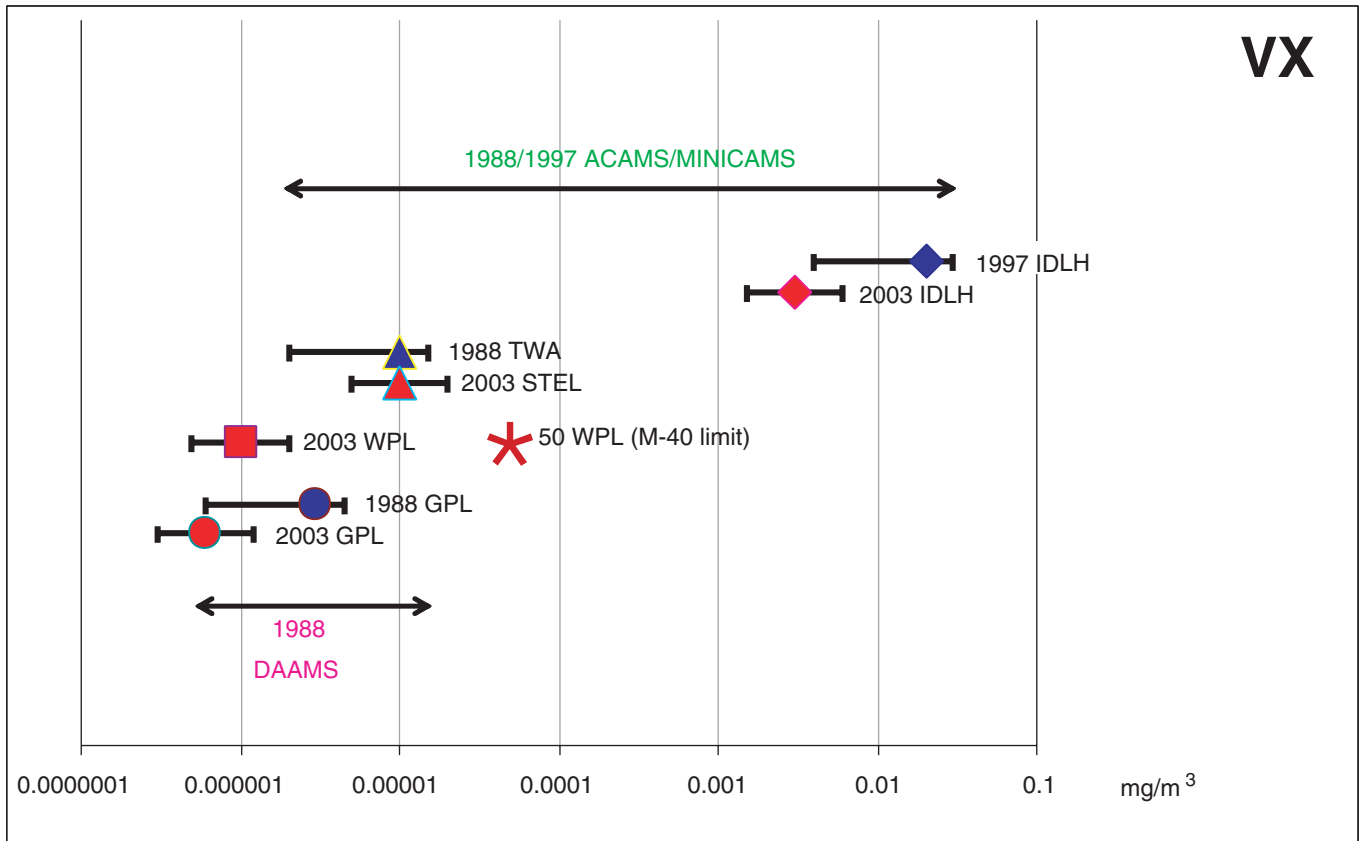


FIGURE 4-3 ACAMS/MINICAMS and DAAMS operating ranges for the 1988/1997 VX AELs and required ranges for the CDC's 2003 VX AELs.

NOTES:

(1) The 1988/1997 AEL concentration ranges for VX over which ACAMS/MINICAMS and DAAMS have been certified and operated for many years at various sites are indicated by horizontal lines that end in arrows. Also represented are the following:

- The IDLH AELs are indicated by diamonds with range bars showing the past concentration range for certifying MINICAMS, 0.20 to 1.50 of the 1997 IDHL value for VX, and the concentration range required in the future, 0.50 to 2.00 of the 2003 IDHL value for VX.
- The CDC's 1988 TWA AEL and the numerically equivalent CDC's 2003 15-minute STEL for VX are indicated by triangles with range bars.
- The CDC's 2003 WPL for VX is indicated by a square with range bars, and the 1988 and 2003 GPLs are indicated by circles with range bars.

(2) The VX concentration limit above which negative-pressure respirators, such as the M40 mask, may not be worn is marked by an asterisk; limits for supplied-air respirators (1,000 WPL) and SCBA (10,000 WPL) are not shown.

SOURCE: NRC, 2005.

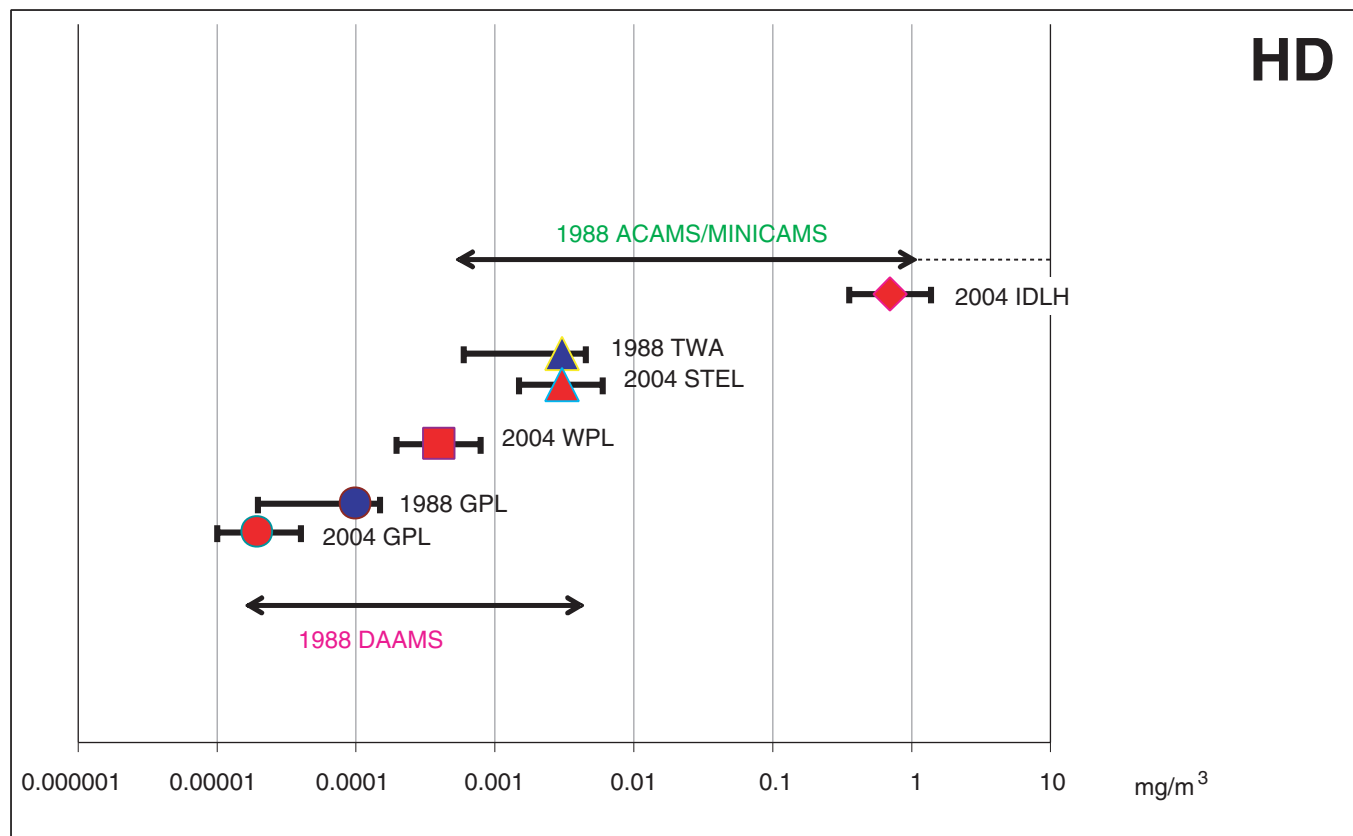


FIGURE 4-4 ACAMS/MINICAMS and DAAMS operating ranges for the 1988 HD AELs and required ranges for the CDC’s 2004 HD AELs.

NOTES:

(1) The 1988 AEL concentration ranges for HD over which ACAMS/MINICAMS and DAAMS have been certified and operated for many years are indicated by horizontal lines that end in arrows. Also represented are the following:

- The “1988 MINICAMS” line includes a dotted line to its right to indicate that even though an IDLH AEL for HD was not defined until recently, MINICAMS has been used for many years to monitor for HD at concentrations up to and far above the CDC’s 2004 IDLH AEL for HD.
- The CDC’s 2004 IDLH AEL for HD is indicated by a diamond with range bars showing the concentration range required in the future when certifying MINICAMS, 0.50 to 2.00 of the 2004 IDLH.
- The CDC’s 1988 TWA AEL and the numerically equivalent CDC’s 2004 15-minute STEL for HD are indicated by triangles with range bars.
- The CDC’s 2004 WPL is indicated by a square with range bars, and the 1988 and 2004 GPLs are indicated by circles with error bars.

(2) Limits for supplied-air respirators (1,000 WPL) and SCBA (10,000 WPL) are not shown.

SOURCE: NRC, 2005.

TABLE 4-1 False-Positive Alarm Rates in 2003 and 2004 for TOCDF ACAMS During VX Operations

| Measurement Periods        | Number of ACAMS Displaying False-Positive Alarms | Number of ACAMS False-Positive Alarms per Day |
|----------------------------|--|---|
| March 2003-April 2003      | 80   | 1.3   |
| December 2003–January 2004 | 99   | 3.1   |
| March 2004–May 2004        | 34   | 0.4   |
| July 2004                  | 73   | 2.4   |

SOURCE: Data from Jeff Kiley, Monitoring Office, Risk Management Directorate, CMA, briefing to the committee, October 5, 2004.



sampling-and-analytical cycles per month (based on the continuous operation of 112 ACAMS with 5-minute cycles). As shown in Table 4-1, the average number of ACAMS false positives is both highly variable and non-negligible, ranging from 0.4 to 3.1 per day. Each false-positive alarm may both disrupt disposal operations and contribute to a “crying wolf” mind-set that may cause staff to discount alarms resulting from an actual agent excursion or release (NRC, 2002).

During a recent 12-month period, 8,237 primary DAAMS samples were collected and analyzed at the VX GPL at TOCDF. Of these samples, VX concentrations greater than 0.20 GPL (the reportable limit for TOCDF) were found for 16 samples. Backup DAAMS tubes for these 16 samples, collected at the same time as the primary samples, were then analyzed using a DAAMS confirmation method, and it was determined that the apparent VX response for each of the 16 tubes was not caused by VX.<sup>8</sup>

The Aberdeen Chemical Agent Disposal Facility (ABCDF) used neutralization to destroy agent HD, which results in the generation of a sulfur-containing decomposition product, thiodiglycol. The ACAMS FPD cannot be used to monitor for HD in an environment that may contain large quantities of a potential sulfur-containing interferent (thiodiglycol). For this reason, MINICAMS monitors configured with an XSD are used for NRT monitoring at the ABCDF. The XSD is sensitive only to halogen atoms in molecules. Thus, a MINICAMS configured with an XSD can detect HD but cannot detect thiodiglycol. A recent communication from the ABCDF disposal site indicated that only about five false alarms were experienced over a recent 18-month period of operation of MINICAMS/XSD systems at the ABCDF, with the alarm level set at 0.70 STEL (equal to 0.70 of the 1988 TWA) and out of more than 8 million instrument cycles—55 instruments × 12 cycles per hour × 24 hours per day × 30 days per month × 18 months.<sup>9</sup> DAAMS monitors at the ABCDF are configured with an MSD, and some monitors also include an FPD. However, the FPD cannot be used for routine HD analysis because of the frequent occurrence of false positives. Thus, most DAAMS samples are analyzed using the MSD.

In past reports, NRC committees have suggested that the Army improve the reliability of ACAMS monitors (NRC, 1994, 1999, 2001, 2002). This committee was provided with data on malfunctions at TOCDF that are considered representative of a typical week of ACAMS monitoring at the STEL level for GB and VX. For the week of September 5-12, 2004, ACAMS monitors for VX at the STEL level experi-

enced 602 instrument cycles in error (malfunction) out of 219,744 total cycles. ACAMS monitors for GB at the old TWA (new STEL) level experienced 194 instrument cycles in error out of 194,880 total cycles.<sup>10</sup> These data do indicate that the ACAMS false-positive alarm rate has been reduced at TOCDF since prior NRC reviews (NRC, 1999).

**Finding 4-1.** The Army has taken significant steps to reduce the level of false alarms (false positives) for ACAMS and MINICAMS monitors at stockpile disposal sites, especially through the elimination of potential chemical interferences and by the adjustment of alarm levels (while still maintaining a statistical response rate of 95 percent or better for the detection of agent excursions above 1.00 STEL). False-positive alarms are still a problem, however, especially when monitoring at VX STEL levels using NRT monitors. Also, false positives are expected to be a significant problem when using DAAMS monitors equipped with FPDs to monitor at the 2003/2004 WPLs and GPLs.

**Finding 4-2.** In accordance with the determinations of previous NRC studies (NRC, 1999, 2001), the committee finds that the reliability of ACAMS, MINICAMS, and DAAMS appears to provide sufficient airborne agent monitoring capability to afford adequate protection to workers, the general public, and the environment.

## ASSESSMENT OF CURRENT AIR MONITORING SYSTEMS

### Assessment of ACAMS and MINICAMS Monitors

#### *Instrument Capabilities*

The Army is now using ACAMS and MINICAMS at stockpile sites to monitor for GB, HD, and VX at the CDC’s 2003/2004 STEL AELs and, when necessary, at the IDLH AELs. At the four incinerator sites, ACAMS are also used to monitor agent levels in the exhaust flows through the pollution abatement systems and the common stack at the source emission limit (SEL), which is equal to the prior allowable stack concentration (ASC) limit (NRC, 2001) and is moderately higher than the new STEL values for each agent (U.S. Army, 2004c). DAAMS monitors are used at stockpile sites for historical monitoring at the CDC’s 2003/2004 WPLs and GPLs and to confirm or deny ACAMS and MINICAMS alarms at the CDC’s 2003/2004 STELs (equal to the CDC’s 1988 TWA AELs).

One other application of ACAMS and MINICAMS monitors is to ensure that negative-pressure respirators are used properly. According to the Occupational Safety and Health

<sup>8</sup>Statistics for false-positive alarms were provided by Jeff Kiley, Monitoring Office, Risk Management Directorate, CMA, briefing to the committee, Chemical Demilitarization Training Facility, Aberdeen Proving Ground, Md., October 5, 2004.

<sup>9</sup>E-mail from Raj Malhotra, CMA, to Margaret Novack, NRC staff, December 14, 2004.

<sup>10</sup>Data provided to the committee by CMA, September 21, 2004.

Administration (OSHA), an assigned protection factor of 50 should be used for negative-pressure respirators, such as the M40 mask. This means that the M40 mask can be used in environments with GB or VX present at concentrations up to 50 times their WPLs for 8 hours and in environments with agent present at concentrations up to 50 times their STELs for not more than 15 minutes. Because HD has been classified as a carcinogen (by the International Agency for Cancer Research), the concentration limit for the use of negative-pressure respirators for this agent is 1.00 STEL (equal to 7.50 WPL).

The committee expects that the more recently implemented use of ACAMS and MINICAMS to monitor for GB, HD, and VX at the CDC's 2003/2004 IDLH levels, and at the CDC's 2003/2004 STELs (numerically equal to the 1988 TWAs), should prove to be straightforward in view of the generally successful performance of these monitoring systems at the 1988 TWA AELs. Full implementation will require the following:

- Developing and testing a monitoring method for the CDC's new HD IDLH level,
- Making minor modifications of existing IDLH methods for GB and VX (due to changes in these values), and
- Testing the modified methods using ACAMS and MINICAMS monitors.

One major problem for ACAMS and MINICAMS monitors will continue to be the occurrence of false alarms when monitoring at the STEL for VX (equal to the CDC's 1988 TWA value). False alarms caused by phosphorus-containing compounds (e.g., pesticides, phosphorus-containing impurities, degradation products of VX, and so on) are likely to continue unless ACAMS and MINICAMS monitors are reconfigured and/or upgraded to improve their chromatographic resolution and/or to monitor VX directly (rather than as the G-analog). Even with the occurrence of false-positive alarms, many years of operating experience have demonstrated that demilitarization operations can proceed safely as long as all such alarms are rigorously treated as real, until they are not confirmed by DAAMS analyses.

**Finding 4-3.** Air monitoring instrumentation used at stockpile disposal sites has been capable of reliable detection of the 1988 TWA levels for agents, as earlier NRC committees have indicated. These NRT instruments (ACAMS and MINICAMS) are likewise capable of detection at the 2003/2004 STEL and 2003/2004 IDLH levels.

#### *Human Interfacing of Air Monitoring Systems*

The human interfaces for ACAMS and MINICAMS do not appear to the committee to suffer from design deficiencies, with the caveat that future changes must be compatible with

operators' current mental models of the system operation. DAAMS interfaces are in effect the laboratory equipment used to determine the concentration in each DAAMS tube. These interfaces do not appear to have design deficiencies for their current uses. The design of the air monitoring system interface in the control room is part of a larger control system where the operators can call up particular ACAMS and MINICAMS results on their displays. Again, each individual display appears to be adequately designed, but the issue of integrating the information from several instruments has not been addressed.

Currently, the readouts of all ACAMS and MINICAMS are transmitted to the control room by the process data acquisition and reporting system (PDARS) and are displayed in the control room using a custom software interface. Here the results from individual ACAMS and MINICAMS are displayed on a geographic layout of the building, which is good practice for maintaining operator situational awareness. However, the individual ACAMS and MINICAMS displays are primarily character-based—that is, naming each ACAMS or MINICAMS device and giving its current reading and any special-condition codes (e.g., challenge or malfunction) as two-letter codes. Character-based displays are better for conveying detailed information but worse for the situational awareness required in an evolving incident. Color is used to some extent in the display of the building as a character changes from green to red when a threshold is exceeded. Better solutions involving symbols for special-condition codes and the use of color for indicating changes from a previous measurement would help operators to understand the overall situation rapidly and accurately. Detailed character information could then be called up when needed by selecting individual ACAMS or MINICAMS icons.

Training will be crucial to allow operators to make the correct decisions involving the redefined AELs. In particular, the concentration is the same for the old TWA and the new STEL, although they have quite different meanings. These changes need to be internalized by all personnel, particularly those who must make decisions regarding continued operation. It is not enough for an operator to be able to recite the definition and the associated actions: the operator must also be trained in what each concept means and why it is important. As noted above, it may be more difficult for an operator to unlearn a skill than to learn a new skill unrelated to prior experience.

#### **Assessment of the A/DAM System**

The A/DAM system has been used at only a few sites to monitor for GB, HD, and VX at the CDC's 1988 TWA AELs, and for GB and VX at the CDC's 1988 IDLH levels. For this reason, the committee cannot assess the reliability of the A/DAM system, although reliability is an important consideration for continuous NRT monitoring. Because the A/DAM system is based on the same technology as ACAMS,

MINICAMS, and DAAMS, however, the committee expects that the A/DAM system is capable of monitoring for GB, HD, and VX at the CDC's 2003/2004 IDLH levels and STELs (equal to the CDC's 1988 TWAs). If future tests of the A/DAM system demonstrate significantly improved selectivity compared with that from ACAMS and MINICAMS monitors and satisfactory reliability, the use of the A/DAM system for critical applications such as stack monitoring may justify the higher cost and complexity of the system.

## Assessment of the DAAMS Monitors

### *2003/2004 STEL Confirmation and WPL Monitoring*

The use of DAAMS monitors to confirm or deny ACAMS and MINICAMS alarms at the CDC's 2003/2004 STELs should prove no more difficult than confirming or denying alarms at the CDC's 1988 TWA levels. The CDC's 2003 WPL for GB is greater than its 1988 GPL for GB and greater than its 1988 TWA level for VX—concentrations that have been monitored using DAAMS for many years. Thus, with respect to sensitivity, it should be possible to use current DAAMS techniques to monitor for GB at the CDC's 2003 WPL, with only minor modifications. Similarly, because the CDC's 2004 WPL for HD is greater than its 1988 GPL for HD, which has also been monitored using DAAMS for many years, only relatively minor changes should be necessary with respect to sensitivity to allow DAAMS to monitor for HD at the CDC's 2004 WPL. These statements assume that the sampling period for DAAMS monitors, when sampling at the WPLs, is no less than 8 hours. (The typical DAAMS sample period used currently for GPL sampling is 12 hours.)

The response of the DAAMS FPD to sulfur-containing compounds, such as HD, is approximately quadratic, since the chemiluminescence detected is due to  $S_2^*$  and each HD molecule contains only one S atom. Thus, although current DAAMS monitors configured with FPDs appear to have adequate sensitivity to monitor at the CDC's 2004 WPL for HD, the signal obtained will be about 50 times less than for the CDC's 1988 TWA AEL (for the same sample volume). Because the concentrations of potential chemical interferences in the environments being sampled will, of course, be unaffected by changes in the regulatory limits for HD, it is likely that a much greater rate of false positives will be observed when using DAAMS monitors for HD at the CDC's 2004 WPL rather than at the CDC's 1988 TWA AEL.

The V-to-G-analog conversion method is routinely used when sampling for VX. Concentration ranges for 1988 DAAMS methods for VX are shown in Figure 4-3. The CDC's 2003 WPL value for VX is less than its 1988 GPL for VX, but falls within the concentration range over which DAAMS methods must be certified for monitoring at the CDC's 1988 VX GPL. Detection limits for VX for 1988 DAAMS methods have been reported to be as low as

30 pg.<sup>11</sup> For a sample flow rate of 1 liter per minute, a sample period of 8 hours, and a concentration of 1.00 WPL for VX (1 picogram per liter), 480 pg of VX would be sampled. This mass is about 16 times greater than the lowest detection limit reported. Thus, with respect to instrument sensitivity, it appears that 1988 DAAMS methods can be modified to reliably determine VX at the CDC's 2003 WPL.

It is anticipated, however, that interference problems are likely to be much greater when using DAAMS methods based on V-to-G-analog conversion to monitor at the CDC's 2003 VX WPL than at the CDC's 1988 TWA level for VX, which is 10 times greater than the CDC's 2003 WPL for VX. The types of interferences expected are those caused by hydrocarbons, sulfur-containing compounds, and phosphorus-containing precursors, impurities, or hydrolysis and decontamination products.

### *2003/2004 GPL Monitoring*

The use of DAAMS to monitor at the CDC's 2003 GB GPL concentration should be relatively straightforward with respect to sensitivity. The phosphorus-equivalent concentration for GB at the CDC's 2003 GPL is only about 33 percent less than the phosphorus-equivalent concentration for VX at the CDC's 1988 GPL, which has been monitored successfully using DAAMS monitors for many years. It is anticipated, however, that the occurrence of false positives for GB GPL monitoring will increase compared with those experienced when using DAAMS to monitor at the CDC's 1988 VX GPL.

The use of DAAMS to monitor at the CDC's 2003 VX GPL will be problematic. The 2003 VX GPL level is 5 times less than the 1988 VX GPL. Although it is anticipated that DAAMS monitors will be sensitive enough to detect VX at this concentration, the probability of false positives is expected to increase significantly.

The use of DAAMS monitors configured with an FPD to determine HD at the CDC's 2004 GPL may be extremely difficult. Although DAAMS monitors have been used successfully at the CDC's 1988 GPL level for HD, the 2004 GPL for this agent is 5 times less, and the signal obtained from the FPD in the DAAMS GC will be 25 times less, compared with the signal obtained when monitoring at the 1988 GPL. It is therefore likely that the sensitivity of an FPD-based DAAMS will be insufficient to monitor at the 2004 HD GPL level and likely that the occurrence of false positives will be significant.

If interferences (false positives) increase for the CDC's 2004 HD WPL and HD GPL—compared with the CDC's 1988 AELs for HD—installing an XSD in the DAAMS GC

<sup>11</sup>Letter from Michael McNaughton, Southwest Research Institute, to John Decker, Centers for Disease Control and Prevention, June 28, 2002.

in place of or in addition to the FPD may provide a resolution to this problem. The XSD has a linear response to HD, is more sensitive to HD than the FPD is, and has less susceptibility to false positives from hydrocarbons than the FPD does. On the other hand, the XSD is susceptible to false positives caused by the presence of chlorine-containing compounds in the area being monitored, and the XSD requires more maintenance than the FPD (as evidenced, for example, by the fact that the manufacturer of the XSD for use with MINICAMS provides a replacement reactor-probe assembly with this detector).

During the past 3 years, the CMA has conducted research and development with the goal of improving DAAMS methods to enable monitoring for GB and VX at the CDC's 2003 WPL and GPL concentrations. The new DAAMS equipment and methods have successfully passed laboratory P&A studies for these agents and concentrations. The results of field P&A studies, however, have been mixed. Field P&A studies have been passed for 4-day tests using 1-hour and 12-hour DAAMS samples at WPL levels. For 12-hour GPL DAAMS samples, however, P&A studies using a GC/FPD-based system passed for GB but failed for VX. P&A studies using a GC/MSD to analyze 12-hour GPL DAAMS samples passed for GB and VX, but with some difficulty. The failure and difficulties experienced during P&A studies for 12-hour GPL DAAMS samples were caused by the presence of intermittent chemical interferences in the areas being monitored.<sup>12</sup>

**Finding 4-4.** DAAMS has proven effective in monitoring at the CDC's 1988 TWA and GPL levels at stockpile disposal sites for more than 15 years. Because the 2003/2004 STELs have the same numerical concentration values as the 1988 TWA levels, historical and confirmation monitoring of GB, VX, and HD at the new STELs using DAAMS will be no more difficult than monitoring these agents at the 1988 TWA levels. Also, monitoring at the 2003 WPL for GB using DAAMS will be straightforward, with no significant increase in the occurrence of false positives (compared with DAAMS monitoring for GB at the 1988 TWA level). However, although DAAMS either has or is likely to have adequate sensitivity for monitoring at 2003/2004 AELs, the frequency of false positives is expected to increase in the following cases:

- The 2003 VX WPL, which is less than the 1988 GPL for this agent;
- The 2004 HD WPL, which is less than the 1988 GPL;
- The 2003 GB GPL level, which is one-third of the 1988 GPL level;

- The 2003 GPL for VX, which is one-fifth of the 1988 GPL value; and
- The 2004 GPL for HD, which is one-fifth of the 1988 HD GPL value.<sup>13</sup>

Potential upgrades to existing air monitoring systems used at stockpile sites are addressed in the next section of this chapter.

## ENHANCEMENTS TO EXISTING TECHNOLOGIES FOR MONITORING AT THE CDC'S 2003/2004 AIRBORNE EXPOSURE LIMITS

To monitor at the new CDC-recommended STEL levels for airborne chemical agents, automated monitoring systems intended for use in the stockpile disposal program must be capable of determining VX concentrations as low as 0.9 parts per trillion by volume, GB concentrations as low as 16 parts per trillion, and HD concentrations as small as 456 parts per trillion. Manual monitoring systems must be capable of the determination of GPL VX concentrations as low as 0.05 parts per trillion, GB concentrations as low as 0.16 parts per trillion, and HD concentrations as low as 3 parts per trillion. In addition, automated and manual monitoring systems must meet stringent quality assurance/quality control requirements and must operate continuously and reliably.

Incremental improvements to the currently available commercial monitoring systems, which rely on sorbent-based sampling and temperature-programmed gas chromatography, are most likely to achieve improvements in airborne chemical agent detection sensitivity and specificity within a 1- to 2-year time frame. Monitoring systems based on these technologies include ACAMS, MINICAMS, and DAAMS, which have been described and evaluated in this report. The NRT monitor known as the A/DAM system, which is essentially an automated version of DAAMS, was also described in the recent non-stockpile report on air monitoring (NRC, 2005). The A/DAM system, however, although a more flexible analytical system than ACAMS or MINICAMS, has had little use in the stockpile disposal program because the A/DAM system is complex, heavy, and costly, compared with ACAMS and MINICAMS.

There are currently no commercially available automated or manual analytical systems other than those listed above that have demonstrated the capability to meet the monitoring requirements of the stockpile disposal program. Most agent detection technologies currently under development are generally targeting the homeland defense market and thus

<sup>12</sup>Monitoring Technology Update, by Jeff Kiley, Monitoring Office, Risk Management Directorate, CMA, briefing to the committee, Chemical Demilitarization Training Facility, Aberdeen Proving Ground, Md., October 5, 2004.

<sup>13</sup>As a consequence of the quadratic response of the FPD, the detector signal for the 2004 HD GPL will be 25 times less than the detector signal obtained for the 1988 HD GPL (for the same sample flow rate and sample period). For this reason, it may prove very difficult to monitor for HD at the 2004 GPL.



are focused on the detection of airborne agent concentrations near or a little less than the CDC's IDLH AELs. Thus, the concentrations of interest to most developers are several orders of magnitude greater than the STEL, WPL, and GPL AELs of interest in the chemical stockpile program.

There are incremental improvements to the current monitoring systems that are under development or currently available. For example, the CMA has sponsored research during the past 3 years that is expected to result in improvements in the sensitivity and selectivity of DAAMS monitors.<sup>14</sup> The DAAMS improvements tested by the CMA included optimizing sample collection, using helium in place of nitrogen as the carrier gas, using a cryotrap to improve resolution and sensitivity, using a Dean's heart-cut switch<sup>15</sup> to improve the separation of agents from potential chemical interferences, optimizing the selection of GC columns to improve peak shape and chromatographic resolution, and so on. However, as noted in the findings presented in the previous section of this chapter, it is unclear whether the improvements under development will result in sufficient DAAMS selectivity to avoid significant levels of false positives when monitoring at the CDC's 2003/2004 GPL levels.

Although the CMA has begun to monitor at the CDC's 2003/2004 WPL concentrations using DAAMS, the agency recently sponsored an evaluation of three automated NRT air monitoring systems for the detection of VX, GB, and HD at WPL levels. The three NRT systems tested were an ACAMS equipped with an FPD, a MINICAMS equipped with a pulsed FPD (PFPD), and an A/DAM equipped with an FPD. Each NRT system was also configured with a front-end, high-volume sampler. Even with the high-volume sampler, the sensitivity of the ACAMS proved insufficient to monitor at the WPLs. Both the MINICAMS and the A/DAM systems passed 4-day P&A studies and 20-day baseline-study tests conducted in laboratories. Each of these two systems was then tested at a stockpile disposal plant. Although both systems passed a 4-day field P&A study for each of the three agents, the A/DAM system failed the 20-day field baseline studies for the three agents because of poor precision and calibration drift. The MINICAMS passed a 4-day field P&A study for each agent and also passed 20-day field

baseline studies for GB and VX, but failed the baseline study for HD because of poor recovery.<sup>16</sup>

A number of possible enhancements applicable to the current air monitoring systems used at stockpile sites represent mature technologies that deserve consideration by CMA. These are addressed briefly in the following paragraphs.

The sensitivity of the FPD is directly proportional to the solid angle defined by the light source (that is, the flame) and the area of the light-sensitive surface (photocathode) in the photomultiplier tube (PMT). The sensitivity of the FPD may be increased by installing a convex lens between the flame and the PMT to increase the solid angle from which light is collected and to focus light onto the photocathode of the PMT. As an example, in a recent DAAMS study, the installation of a convex lens between the flame and the PMT resulted in an increase in the signal-to-noise ratio by about a factor of five (FOCIS, 2004). This modification is inexpensive and relatively simple to implement. An improvement in the signal-to-noise ratio may be especially important when using DAAMS to monitor at the CDC's 2003/2004 GPLs.

Although cryotrap traps have been used to decrease eluted peak widths on GC/MSD-based DAAMS confirmation systems at stockpile disposal sites, cryotrap traps have not been used for routine DAAMS analysis by GC/FPD-based systems. A cryotrap is generally installed so that a short length of the front end of the GC's analytical column can be cooled—using a tank of compressed, liquid carbon dioxide; chemical compounds entering the column are thus trapped in a narrow band. Alternatively, cryotrap traps may be cooled by a Peltier-based cooling system. A cryotrap may be heated ballistically to release the trapped chemicals to allow them to be separated before entering the detector. In a recent study, the peak widths for GB and the G-analog of VX obtained in a DAAMS were decreased and the heights of the peaks were increased by a factor of about four by the use of a cryotrap installed at the front end of the analytical column (FOCIS, 2004).

A PFPD is somewhat more selective and more sensitive than an FPD (Frischman and Amirav, 2000). This detector exhibits fewer false positives caused by hydrocarbons than the FPD does. The PFPD, however, is more expensive and more complex than the FPD to operate and maintain, and the PFPD will not reduce the frequency of interferences caused by phosphorus-containing compounds such as organophosphorus pesticides.

The XSD is more sensitive to HD than the FPD is, and the response of the XSD is linear (compared with the quadratic response of the FPD in the sulfur-specific mode). The

<sup>14</sup>Monitoring Technology Update, by Jeff Kiley, Monitoring Office, Risk Management Directorate, CMA, briefing to the committee, Chemical Demilitarization Training Facility, Aberdeen Proving Ground, Md., October 5, 2004.

<sup>15</sup>The key component of the heart-cut system is a Dean switch, which allows the effluent of the precolumn to be directed into the analytical column only during a short period, from the time just before the agent of interest begins to exit the precolumn to the time just after the agent has exited the precolumn. At all other times before and after this agent window, the carrier-gas effluent from the precolumn vents through a restrictor column to the atmosphere (or to a second detector installed to monitor the effluent from the precolumn). The liquid phase of the analytical column generally differs greatly in polarity from the liquid phase of the precolumn.

<sup>16</sup>Monitoring Technology Update, by Jeff Kiley, Monitoring Office, Risk Management Directorate, CMA, briefing to the committee, Chemical Demilitarization Training Facility, Aberdeen Proving Ground, Md., October 5, 2004.

addition of an XSD to DAAMS may better enable the detection of HD at the CDC's 2004 WPL and GPL AELs for this agent. Also, the XSD, which detects molecules based on their halogen atoms, may result in fewer false positives compared with those from the FPD because there are few naturally occurring chlorinated compounds versus a large number of naturally occurring sulfur-containing compounds (potential interferences). XSD-based MINICAMS monitors have been used successfully to monitor for HD at the ABCDF site, Aberdeen Proving Ground, Maryland.<sup>17,18</sup>

Sulfur chemiluminescence detectors (SCDs) use a hydrogen flame to produce SO from sulfur-containing analytes and react the SO with ozone to produce electronically excited SO<sub>2</sub><sup>\*</sup>, producing radiation near 340 nm (Benner and Stedman, 1989). SCDs have generally replaced the use of FPDs in the determination of low levels of sulfur-containing compounds in many complex analytical matrices (Sherer et al., 1990; Benner and Stedman, 1991). SCDs typically have a minimum detection limit of about 1 picogram of S per second versus about 100 picograms of S per second for the FPD, and the SCD is typically about 10,000 times more selective with respect to hydrocarbon interferences than the FPD is. Also, the response of the SCD is linear over about 4 to 5 orders of magnitude compared with the quadratic response of the FPD for sulfur-containing compounds. Commercial SCDs were developed specifically for and have been used successfully as detectors for GC systems for more than 15 years (Sherer et al., 1990).

All of the suggested enhancements to ACAMS, MINICAMS, and DAAMS presented above are mature technologies that have been used as accessories for GC systems for many years. There is one published technology that has not yet been fielded commercially as a GC detector but that may be worth considering for use in agent monitoring applications. This technology is a magnetically quenched FPD (Wakayama et al., 1987). In this FPD, the flame is located in a strong oscillating magnetic field, and the signal from the photomultiplier tube is detected using a lock-in amplifier. HPO<sup>\*</sup> emissions are quenched by the strong magnetic field. HPO<sup>\*</sup> emissions can be detected readily as a signal with the same frequency as that of the oscillating magnetic field. Emissions caused by the presence of chemical interferences (e.g., hydrocarbons and sulfur-containing compounds) will not be detected because S<sub>2</sub><sup>\*</sup> emissions and hydrocarbon emissions are not quenched by the magnetic field.

The development and testing of a fieldable magnetically quenched FPD are still in the development stage. This detector has the potential to become the most selective FPD

for the detection of organophosphorus compounds such as GB and VX (compared with the conventional FPD and the PFPD). Nonetheless—as in the case of the FPD and the PFPD—the magnetically quenched FPD will not resolve interferences caused by phosphorus-containing compounds, such as organophosphorus pesticides.

**Finding 4-5.** The efforts of the Chemical Materials Agency (CMA) have resulted in the demonstration of significant incremental improvements in MINICAMS and DAAMS. It is clear, however, that even with the improvements demonstrated by the CMA, it will probably be difficult to monitor agents, especially VX and HD at the 2003/2004 GPL levels, without a significant increase in false positives (compared with monitoring at the 1988 GPL levels). Also, despite the success demonstrated to date, false positives may be a significant problem when monitoring at the 2003/2004 WPLs. Finally, false positives for ACAMS and MINICAMS monitors, especially when monitoring at the STEL for VX, are expected to continue.

**Recommendation 4-5.** The Chemical Materials Agency (CMA) should consider a wider range of incremental improvements to ACAMS, MINICAMS, and DAAMS to allow these monitoring systems to better monitor at the CDC's 2003/2004 AELs. Some technologies that deserve consideration by the CMA include the following:

- Adding a convex lens to the FPD to improve the signal-to-noise ratio of this detector in ACAMS, MINICAMS, and DAAMS;
- The use of cryotrap for all DAAMS monitors to sharpen GC peaks and thereby improve selectivity and sensitivity;
- The equipping of DAAMS systems with a PFPD in place of the FPD to enhance the selectivity and sensitivity of the DAAMS when monitoring for GB, VX, and HD;
- The equipping of DAAMS monitors with an XSD to enhance the selectivity and sensitivity of this system when monitoring for HD;
- The use of an SCD for the detection of HD; and
- Funding the development of a phosphorus-specific FPD based on the magnetic quenching of HPO<sup>\*</sup> emissions, a detector that is expected to be much more selective for organophosphorus compounds than is the conventional FPD or the PFPD.

## ALARM LEVELS FOR NEAR-REAL-TIME MONITORS

This section examines the CDC's recommendations and the Army's written guidance regarding alarm levels for NRT monitoring systems. (See also Box 4-1.) Some of the issues presented here are described in more detail in the NRC's recent report on air monitoring within the non-stockpile program (NRC, 2005).

<sup>17</sup>Assembled Chemical Weapons Alternatives Chemical Agent Monitoring, by Craig Myler, Bechtel, chief scientist, Pueblo Chemical Agent Destruction Pilot Plant, briefing to the committee, Washington, D.C., Keck Center of the National Academies, November 22, 2004.

<sup>18</sup>E-mail from Raj Malhotra, CMA, to Margaret Novack, NRC staff, December 14, 2004.

### BOX 4-1 Monitor Set Points and False Alarm Rates

Each automated and manual monitoring system (and its associated written methods) used at stockpile disposal sites must meet quality assurance/quality control requirements for baseline studies that consist of daily 1.00-AEL challenges. Because of errors inherent in any instrument system, agent concentrations reported by NRT monitoring systems (i.e., found concentrations) are generally not in agreement with the true concentrations of agents in areas being monitored. This problem is addressed by requiring that NRT monitoring systems must yield found concentrations in the range of 0.75 to 1.25 AEL 95 percent of the time to pass a baseline study. If this requirement cannot be met, the alarm level for the NRT system must be set so that 95 percent of all 1.00-AEL challenges result in an alarm, and at least 75 percent of daily 1.00-AEL challenges must yield found concentrations in the range of 0.75 to 1.25. For manual monitoring systems, the reportable limit must be set so that 95 percent of daily 1.00-AEL challenges yield found concentrations greater than or equal to the reportable limit.

The requirement that an alarm will be sounded at least 95 percent of the time for any NRT monitoring system that is challenged at a true concentration of 1.00 AEL has usually resulted in site-specific alarm levels in the range of about 0.2 to 0.5 AEL, and each monitoring system at a given site that is properly operated and maintained sounds an alarm at least 95 percent of the time that an excursion of agent at a true concentration at or above 1.00 AEL takes place.<sup>1</sup>

Statements in the CDC's 2003/2004 Federal Register announcements (Federal Register, 2003, 2004) and the first method for setting NRT alarm levels listed in the CMA's *Programmatic Laboratory and Monitoring Quality Assurance Plan* (U.S. Army, 2004a), however, indicate that it is acceptable to set the alarm level for an NRT system to 1.00 AEL, as long as the first-challenge pass rate is  $\geq 95$  percent. If the alarm level is set to 1.00, however, an NRT monitoring system will detect true agent excursions above 1.00 AEL and sound an alarm only 50 percent of the time, no matter how accurate the concentration data reported and no matter what the value of the first-challenge pass rate is (for an unbiased, normal distribution).

The alarm level determines the probability that an alarm is sounded any time the true agent concentration in an area being monitored equals or exceeds 1.00 AEL. The lower the alarm level, the higher the probability of detecting such excursions. For example, for an alarm level set at 0.20 AEL, ACAMS or MINICAMS monitors typically have a probability of about 99 percent of sounding an alarm for an agent excursion above 1.00 AEL. Setting the alarm level at 0.20 AEL does not mean that the Army has, in effect, lowered the concentration of interest from 1.00 AEL to 0.20 AEL. The purpose of setting the alarm level at 0.20 AEL is to ensure a high probability of sounding an alarm any time that the true agent concentration in an area being monitored exceeds 1.00 AEL. Thus, the setting chosen for the alarm level is based on the desired degree of confidence in sounding an alarm and the distribution of found concentrations obtained for 1.00-AEL challenges. The alarm level has no impact on the calibration or daily operation of the NRT monitoring system. The Army must negotiate alarm levels for each disposal facility with the relevant state regulatory agency, and these alarm levels are typically specified in the facility's operating permit.

The setting chosen as the alarm level does have an impact on the probability of false negatives and the probability of false positives. For example, if an alarm level of 0.50 is chosen, ACAMS or MINICAMS monitors typically sound an alarm for true agent concentrations of 1.00 AEL at least 95 percent of the time, and an alarm fails to be sounded for this concentration less than about 5 percent of the time. For this example, the false-negative rate would be about 5 percent. On the other hand, for an alarm level set at 0.50, true agent concentrations of 0.50 AEL would result in an alarm about 50 percent of the time, and true agent concentrations of 0.80 AEL would result in an alarm about 69 percent of the time for a normal, unbiased distribution. These alarms, however, would be considered false positives because, although such an alarm results from the detection of agent, the true concentration of agent is less than the regulatory limit of 1.00 AEL. Data collected on found concentrations during P&A studies may be used to determine the proper settings for alarm levels to achieve a given probability of sounding an alarm for true agent concentrations at or above 1.00 AEL, and to enable determination of false alarm rates for various true agent concentrations and various alarm-level set points.

Another type of false positive is the apparent detection of agent owing to the presence of chemicals in the area being monitored that results in positive signals from the NRT monitoring system. Such false positives may be reduced by raising the alarm level, but the rate of false negatives for the detection of 1.00-AEL concentrations of agent will also increase.

As an example of an action that has resulted in a reduction in false alarms, the Army recently obtained approval from the State of Utah to increase the alarm set point from 0.2 to 0.5 when using ACAMS to monitor at the VX old TWA/new STEL level at TOCDF. This action reduced the false alarm rate by about a factor of three while still maintaining a statistical response rate of 95 percent for true VX concentrations of 1.00 TWA for all operational ACAMS at the TOCDF site.<sup>2</sup>

<sup>1</sup> The alarm level for all NRT monitoring systems at a given site is typically set to the same value, and the value is chosen so that all monitoring systems that are properly operated and maintained sound an alarm at least 95 percent of the time that the true agent concentration equals or exceeds 1.00 AEL.

<sup>2</sup> Statistics for False-Positive Alarms, by Jeff Kiley, Monitoring Office, Risk Management Directorate, CMA, briefing to the committee, Chemical Demilitarization Training Facility, Aberdeen Proving Ground, Md., October 5, 2004.

Some of the issues raised in this section of Chapter 4 regarding alarm levels for NRT monitoring systems also apply to reportable limits for manual monitors such as DAAMS.<sup>19</sup> The committee chose to limit the discussion presented here to NRT monitoring systems because (1) more than 90 percent of the monitoring data generated at stockpile sites are obtained using NRT monitors; (2) alarm levels are most critical for NRT monitors, which are expected to provide an immediate warning to workers; (3) events causing positive DAAMS results are likely to have been detected by other means or corrected by the time DAAMS samples are analyzed; and (4) it is a simple matter to extract the key points in the discussion above and apply them to manual (DAAMS) monitoring.

Before discussing alarm levels for NRT monitors, it is important to review the following terms:

- *Alarm level.* A predetermined value for an NRT method that, when equaled or exceeded, will result in an audible and/or visual alarm at the location of the NRT monitor. The alarm level must be set so that the statistical response rate at the alarm level is greater than or equal to 95 percent (U.S. Army, 2004a).
- *Action level.* A predetermined value, usually for an NRT method, that, when equaled or exceeded, indicates the need to conduct a series of required actions in response to the apparent detection of agent. An action level is typically less than the alarm level for an NRT monitor. Actions taken when the action level is exceeded (but the alarm level is not exceeded) may include checking to ensure that the NRT monitor is functioning properly, locating and correcting a leak before the concentration of agent at the location being sampled exceeds the alarm level, and so on.<sup>20</sup>

The CDC's 2003 Federal Register announcement regarding AELs for G and V nerve agents states (Federal Register, 2003, p. 58349):

In implementing the WPLs, STELs, and GPLs, specific reduction factors for statistical assurance of action at the exposure limits are not needed because of safety factors already built into the derivation of the exposure limit. This

<sup>19</sup>Reportable limit: "A predetermined value for a historical method that, when equaled or exceeded, will be reported as chemical material that may have exceeded the monitoring level" (U.S. Army, 2004a, p. B-9). For a Class I historical method (that is, a manual method such as DAAMS), the reportable limit must be set so that the statistical response rate at the reportable limit is greater than or equal to 95 percent (that is, the probability, expressed as a percentage, that a 1.0-AEL Quality Plant challenge will generate a response greater than or equal to the reportable limit, must be greater than or equal to 95 percent) (U.S. Army, 2004a).

<sup>20</sup>Personal communication between Robert Durgin, chief, Monitoring Team, CMA; Jeff Kiley, Monitoring Office, Risk Management Directorate, CMA; and Gary Sides, committee member, on November 30, 2004.

recommendation assumes that the sampling and analytical methods are measuring within  $\pm 25$  percent of the true concentration 95 percent of the time. If this criterion is not met, an alarm level or action level below the exposure limit may be required.

The CDC's 2004 Federal Register announcement addresses airborne exposure limits for HD and includes the following statement (Federal Register, 2004, p. 24167):

Although the CDC does not specifically recommend additional reduction factors for statistical assurance of action at the exposure limit, exposures to sulfur mustard should be minimized given the uncertainties in risk assessment, particularly as related to characterizing carcinogenic potency.

No guidance regarding alarm or action levels for HD are included in the 2004 Federal Register announcement.

The Army's latest version of its *Programmatic Laboratory and Monitoring Quality Assurance Plan* states that the alarm level for NRT monitors, which are used to monitor at STEL and IDLH concentrations, can be set one of two ways (U.S. Army, 2004a):

- If the first-challenge pass rate is  $\geq 95$  percent for the NRT monitor, the alarm level may be set at 1.00 AEL.<sup>21</sup>
- If a first-challenge pass rate of  $\geq 95$  percent cannot be achieved, the alarm level must be set to a value that results in a statistical response rate of  $\geq 95$  percent and a first-challenge pass rate of  $\geq 75$  percent must be maintained.<sup>22</sup>

The Army has adopted the CDC's 2003/2004 recommendations regarding new AELs for the agents GB, VX, and HD. The Army has also prepared documents providing guidance or specific instructions that must be carried out in the event that the concentration of a given agent in an area being monitored exceeds 1.00 AEL (1.00 STEL or 1.00 IDLH for NRT monitoring systems). These documents include the following:

- *Implementation Guidance Policy for Revised Airborne Exposure Limits for GB, GA, GD, GF, VX, H, HD, and HT*, June 18, 2004 (U.S. Army, 2004b);
- *Programmatic Monitoring Concept Plan*, Final, June 2004 (U.S. Army, 2004c); and
- *Programmatic Laboratory and Monitoring Quality Assurance Plan*, Final, June 2004 (U.S. Army, 2004a).

<sup>21</sup>The first-challenge pass rate is the percentage of 1.00-AEL challenges that pass on the first attempt for each day (that is, the percentage of challenges that yield reported concentrations in the range of 0.75 to 1.25).

<sup>22</sup>The statistical response rate at the alarm level is the probability that a 1.00-AEL first challenge of the NRT monitor will generate a response greater than or equal to the alarm level.



The purpose of an alarm level is to ensure a high degree of confidence that an excursion of the true agent concentration above 1.00 AEL will result in an alarm so that workers can take written required actions in a timely manner to protect themselves, the general public, and the environment. If the alarm level for an NRT monitoring system were set to 1.00 AEL, several potentially serious worker-perception, public-perception, and practical problems will result. These problems include the following:

- The Army has successfully used a statistical approach to setting alarm levels for the past 20 years so as to ensure at least a 95 percent probability of detecting agent excursions at true concentrations equal to or greater than 1.00 STEL/TWA or 1.00 IDLH. Setting alarm levels at 1.00 and thereby reducing the probability of detecting true agent excursions above 1.00 STEL or 1.00 IDLH to 50 percent or less will be difficult to justify.
- Because some instruments may be negatively biased and others may be positively biased, on any given day alarm rates (that is, the percentage of 1.00-AEL challenges that result in an alarm) may vary from 100 percent for some instruments to 0 percent for other instruments. This will lead to the impression that there is a large variation in performance from instrument to instrument.
- Because the bias of a given instrument may vary from day to day or week to week, the alarm rate for a given instrument may vary from 100 percent to 0 percent during a given period of time. This will lead to an impression of widespread instrument instability.
- HD has been classified as a carcinogen by the International Agency for Cancer Research, and the CDC has stated that exposure should be minimized. If the alarm level is set to 1.00 AEL, NRT monitoring systems will fail to sound an alarm 50 percent of the time that the true concentration of HD exceeds 1.00 AEL (for an unbiased, normal distribution). This seems to violate the CDC's requirement that exposure to sulfur mustard should be minimized.

**Finding 4-6.** The Army's plan to allow alarm levels for NRT monitors to be set at 1.00 AEL, especially for the CDC's 2003/2004 STEL and IDLH values, has the potential to be perceived by workers and the general public as a significant reduction in safety for workers; will result in widely varying alarm rates from instrument to instrument and from week to week; will increase the probability that a worker may be exposed to unacceptable levels of HD, a classified carcinogen; and will increase the likelihood that the Army will not respond properly or in a timely manner to the presence of agents at true concentrations above the AELs. The only perceived benefit to raising the alarm level to 1.00 AEL is a possible reduction in the rates of false alarms, but this benefit

is gained at the expense of a higher probability of false negatives.

**Recommendation 4-6.** The Army should consider continuing to use alarm levels that ensure that all properly operated and maintained NRT monitors at a given site have at least a 95 percent probability of sounding an alarm any time the true agent concentration in an area being monitored exceeds 1.00 STEL.

**Finding 4-7.** At some sites, state regulators may insist that alarm levels be set at 0.2 STEL, the lower limit of certification for NRT monitors, even though it is likely that a statistical response rate of 95 percent or better can be achieved with the alarm level set at 0.5 STEL. Although an alarm level of 0.2 STEL typically ensures at least a 99 percent probability of detecting a true agent excursion above 1.00 STEL, alarm levels this low contribute significantly to the frequency of false alarms observed at stockpile disposal sites and contribute to a reduction in worker safety caused by the human tendency to discount an alarm if false alarms are experienced frequently.

## MONITORING DATA ACQUISITION SYSTEMS AT STOCKPILE DISPOSAL SITES

Automated NRT monitors in demilitarization facilities are linked to the plants' process data acquisition and recording system (PDARS), which transmits data to the control room and as well as archiving it for managerial and regulatory use. The PDARS was designed some time ago and has relatively limited data transmission and processing power. Enhancements in automated monitoring system components must be compatible with PDARS interface and bandwidth requirements. Systemization procedures for interfacing automated chemical agent monitors with PDARS and other data acquisition and recording systems are specified in the *Programmatic Laboratory and Monitoring Quality Assurance Plan* (U.S. Army, 2004a).

The results of DAAMS analyses and other nonautomated analytical measurements are recorded by a laboratory information management system (LIMS), which also archives the data. The LIMS used is specific to each demilitarization site, but general guidance is provided by CMA programmatic documents (U.S. Army, 2004a). Since the LIMS is much more easily upgraded and expanded than the PDARS is, enhancements in laboratory-based chemical agent monitoring for confirmation and historical monitoring should not be constrained by limitations in data acquisition and recording systems.

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## 5

# Prospective Innovative Chemical Agent Monitoring Technologies

The challenges of reliably monitoring airborne chemical agents at the very low concentrations required by the airborne exposure limits (AELs) for chemical weapons storage and demilitarization activities are daunting (see Chapter 2). Airborne chemical agent mixing ratios in the range of a few parts per billion (ppb) to hundredths of a part per trillion (ppt) must be measured as quickly as possible, and with high specificity to minimize dangerous false-positive or false-negative detections. The triple constraints of high sensitivity, high specificity, and rapid response place severe demands on any chemical agent monitoring system for demilitarization activities (Hill and Martin, 2002).

Components of the current agent monitoring system (both near-real-time (NRT) alarms and confirmation and historical monitors) described in Chapter 4 achieve high sensitivity by concentrating agent or agent derivatives from large volumes of air onto absorptive cartridges that are subsequently desorbed for analysis. Using gas chromatography, the current systems achieve high selectivity by separating agent or agent-derivative species from potential interferent chemicals. Unfortunately, the concentration and separation steps both take time, so the high sensitivity and selectivity of the current system are achieved at the expense of response rate, which varies from a few minutes for NRT ACAMS and MINICAMS alarms to hours for the DAAMS alarm confirmation and historical measurement system.

As discussed in Chapter 3 in the subsection entitled “Methods of Detection,” advanced monitoring techniques for other trace constituents of the atmosphere are generally based on one of the following:

- *Optical spectroscopy* (absorption or scattering of radiation at specific wavelengths),
- *Mass spectrometry* (ionization followed by mass selective detection), and
- *Chemical sensing* (binding of the analyte at a surface or receptor followed by generation of an optical or electrical signal).

One potential advantage of considering chemical agent measurement techniques based on one or more of these approaches is that they use measurement observables that differ from those exploited by the instruments currently in use. Consequently, these approaches are not subject to the same sources of error or interference, although they may be subject to their own unique sources of error.

A further potential advantage of new chemical agent monitoring technologies that may be developed and deployed to supplement the system currently in use is the possibility of significantly improving response time, which is one of the major weaknesses of the current system. Improvements and enhancements to the components of the current system, as discussed in Chapter 4, promise incremental improvements in sensitivity and selectivity but will do little to improve response time. The goal for any supplementary technology should be to move from NRT (<15 minutes) to real-time (~1 to 10 seconds) measurements at the short-term exposure limit (STEL) or the immediately dangerous to life and health (IDLH) level, without significant loss of sensitivity and specificity.

Over the past two decades, great progress has been made in developing robust, real-time trace chemical measurement systems for deployment at both fixed sites and on mobile platforms for atmospheric chemistry and air quality measurements (Kolb, 2003). Most of these systems are based on optical spectroscopy (in either an open-path or sampling mode), mass spectrometry, or, more recently, molecular-level chemical sensors. These techniques have the potential of providing highly selective, real-time measurements of specific pollutants. In this chapter, techniques that have proven to be effective or promise significant advantages for atmospheric chemistry and air quality measurements are reviewed and evaluated for their potential for innovative airborne chemical agent monitoring.

## OVERVIEW OF OPTICAL DETECTION TECHNOLOGIES

### Basic Principles

A particularly straightforward approach for monitoring trace gases in the atmosphere is the absorption of infrared, visible, or ultraviolet radiation. The spectrum of a molecule provides a distinctive molecular “fingerprint” for the species being sought, and the amount of radiation absorbed at the specified wavelength is directly proportional to the concentration of that species. This contrasts with techniques such as fluorescence, in which corrections for quenching may be required.

The fraction of light transmitted through a vapor column (transmittance  $T$ ) is governed by the Beer-Lambert law,

$$T = (I/I_0) = e^{-N\sigma l} \quad (5-1a)$$

where  $I_0$  and  $I$  are the incident and transmitted light intensities, respectively;  $e$  is the natural logarithm base defined for all positive real numbers;  $N$  is the number density of the absorber (molecules per cubic centimeter);  $\sigma$  is the absorption cross section (square centimeters per molecule); and  $l$  is the path length through the absorbing sample in centimeters. Equation (5-1a) is often written as

$$T = 10^{-ac/l} \quad (5-1b)$$

where  $a$  is the absorptivity and  $c$  is the species concentration. The absorbance  $A$  is defined as  $\log_{10} T = \log_{10} (I/I_0)$ . The absorptivity is absorbance divided by path length times concentration.

A typical cross section for a strong optical transition is  $10^{-18}$  cm<sup>2</sup>. For a linear, single-pass absorption measurement, detector and source noise limit the fractional absorption that can be observed. Using state-of-the-art laser sources, detectors, and signal averaging techniques, a  $\delta I/I_0 = 1 \times 10^{-5}$  Hz<sup>-1/2</sup> has been obtained (Nelson et al., 2002). This sensitivity permits trace gases to be detected at sub-ppb levels in the ambient atmosphere. Achieving such high sensitivity may be problematic for agent molecules, however, which possess congested, poorly resolved spectra. Furthermore, the required monitoring sensitivity at the current AELs is lower than that which can be achieved by single-pass absorption methods.

A number of sensitivity enhancement strategies exist for attaining the required level of detection. The most straightforward is simply to increase the path length, either by enclosing a sample of the atmosphere in a multiple-reflecting cell or extending the path length a long distance through the atmosphere. Off-axis resonator Herriott cells provide 100 to 300 internal reflections, giving an effective path length up to 210 m (Zahniser et al., 1995). In order to use these cells effectively, a highly collimated light beam (such as that from a laser source) is required. These cells require a fairly large sample of gas (about 0.3 liter) due to geometric constraints,

and reflection losses at the mirrors may be as much as 80 percent overall. Long-path measurement through the atmosphere is the basis of differential optical absorption spectroscopy (DOAS) and open-path Fourier transform infrared (FT-IR) spectroscopy. Such measurements integrate over variable concentrations along the optical path, but provide wide coverage in circumstances in which sample collection is difficult or infeasible. DOAS and open-path FT-IR are discussed in more detail below.

An alternative strategy for increasing sensitivity by reducing noise rather than extending path length is frequency modulation (FM) spectroscopy (Werle, 1996). Using FM techniques,  $\delta I/I_0$  can be reduced to a few parts in  $10^7$ , which allows ppb sensitivity to be achieved. There are several limitations to FM spectroscopy, however. To be effective, the modulation amplitude needs to be greater than the line width of the spectroscopic transition, effectively limiting the technique to small molecules at low pressures. FM spectroscopy is not readily applicable to large molecules with congested (inhomogeneously broadened) spectra, such as chemical agents at ambient atmospheric pressure.

Some of the limitations of FM spectroscopy can be overcome by measuring a signal proportional to  $\delta I$  itself rather than to  $\delta I/I_0$ . Two such approaches are photoacoustic spectroscopy (PAS) and cavity ringdown spectroscopy (CRDS). PAS detection uses a sensitive microphone to measure the acoustic response of an absorbing medium to optical energy deposited in the medium. Since the absorbed energy is converted to a temperature increase and thence to a pressure wave by a rapid relaxation process, PAS is well suited to measurements at atmospheric or higher pressures. PAS has been implemented in mobile systems for field monitoring using a variety of laser systems (Sigrist et al., 2001; Nägele et al., 2001; Fischer et al., 2001; Sigrist, 2000), with an equivalent sensitivity of  $\delta I/I_0 \cong 2 \times 10^{-9}$ /cm, allowing atmospheric trace gases to be detected at concentrations of 70 ppt.

CRDS overcomes some of the limitations of using multiple-reflection gas cells (Busch and Busch, 1999). CRDS is based on the principle that when a pulse of light is injected into an optical resonator (or cavity) formed by highly reflective mirrors, the pulse will circulate within the cavity, and the output of the cavity will decay exponentially with time. The decay rate of the circulating intensity within the cavity is dependent on losses at the mirrors (due to their nonperfect reflectivity) and attenuation by any absorber in the cavity. Since the mirror reflectivity is known (either through an empty cavity measurement or from a measurement made off resonance to any absorbers present in the cavity), measuring the exponential decay allows detection of the absorber in the cavity according to the following equation:

$$\text{decay rate} = \frac{1}{\tau} = \frac{c}{L} (\ln R + \alpha L) \quad (5-2)$$



where  $\tau$  is the measured exponential decay half-life (ringdown time) of the CRDS signal,  $\alpha$  is the net absorbance of the analyte molecule,  $L$  is the length of the cavity,  $c$  is the speed of light, and  $R$  is the reflectivity of the mirrors comprising the cavity.

If mirrors of sufficiently high reflectivity ( $R > 99.99$  percent) are available, the light injected into the cavity can make up to  $10^4$  round-trip passes, which translates into an effective absorption path length of tens of kilometers for a cavity length on the order of 1 m. Since absorption signals are directly proportional to the path length of the sample, this technique is thus capable of detecting an absorbance due to a very low density of sample. Pulsed CRDS has been shown to be capable of detecting explosive vapors with an absorption sensitivity of  $2 \times 10^{-8}$  per centimeter, which corresponds to detection of 1.2 ppb of TNT vapor (Todd et al., 2002). In order to achieve such sensitivity, multiple absorption wavelengths must be used, and the high-reflectivity cavity mirrors must be kept clean of contamination, greatly limiting their application for monitoring agents in the atmosphere.

### Long-Path Optical Measurements

DOAS makes use of an extended optical path through the open atmosphere (Plane and Nien, 1992; Evangelisti et al., 1995; Platt, 1994). In addition to eliminating the need for sample handling, DOAS permits real-time, in situ measurements to be made of the path-averaged atmospheric composition. To achieve the required detection sensitivity, the optical path may need to be extended over a distance of a kilometer or more. As noted earlier, the measurement integrates concentration along the beam path. By deploying a set of retroreflectors at strategic locations, multiple directions or elevations can be sampled in a short period of time from a single monitoring station. The measurement must be carried differentially, that is, at pairs of wavelengths on and off resonance with the absorption feature being monitored, in order to discriminate against background absorption and scattering in the atmosphere, especially by particulates and aerosols. A broadband ultraviolet (UV) source is generally used for DOAS measurements.

Among the advantages of DOAS are that broadband features caused by Rayleigh or Mie scattering are discriminated against, there is no need to estimate the spectral background (as there often is for open-path (OP) FT-IR spectroscopy; see below), and it has fairly good specificity. The biggest disadvantage of DOAS is that only a limited number of molecules have suitable absorption bands in the UV-visible spectral region. The UV absorption spectra of chemical agents (GB, HD, VX, and others) generally show weak and featureless absorption below 250 nm (Rewick et al., 1986), resulting in poor sensitivity and poor discrimination from other UV-absorbing atmospheric components. Atmospheric turbulence can also degrade DOAS detection limits. Finally,

certain meteorological conditions (e.g., rain, snow, fog, and clouds) can render the method inoperative.

### Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FT-IR) spectroscopy is an instrumental technique that is commonly used for characterizing solid and liquid samples, but it can also be used for detecting and quantifying the presence of gaseous species in the atmosphere. In OP/FT-IR measurements, a beam of infrared radiation from a blackbody radiation source is modulated by a two-beam interferometer, passed over a path length of between 100 m and 800 m, and measured by an appropriate detector. Certain wavelengths are absorbed by molecules in the atmosphere; these molecules may be chemical agents or other constituents of the atmosphere such as water vapor or volatile organic compounds. The intensity of each feature in the absorption spectrum is proportional to the product of the concentration of the molecule and the path length of the beam. Spectral signatures of a number of chemical agents and simulants have been reported by Hoffland et al. (1985) and Sharpe et al. (2003). Figure 5-1 shows the infrared absorptivity of GB and HD vapor in the 700 to 1400  $\text{cm}^{-1}$  region, which corresponds to an atmospheric transmission window.

In principle, FT-IR spectroscopy could measure the concentration of chemical agents at intervals of less than 5 seconds, but the technique is several orders of magnitude less sensitive than the ACAMS is even when the measurement time is increased to several minutes, since detection limits are generally inversely proportional to the square root of the data acquisition time.

The use of FT-IR for chemical agent monitoring at demilitarization facilities has been suggested.<sup>1</sup> For perimeter (or fence-line) monitoring by OP/FT-IR spectroscopy, the beam from the interferometer would be expanded by a telescope and passed through the open atmosphere over a distance of typically 100 to 400 m to a retroreflector that returns the beam to the telescope and hence to the infrared detector (see Figure 5-2) (Russwurm and Childers, 2002). For such measurements, the analyte is rarely dispersed uniformly over the beam path, and the path-integrated concentration is measured. Alternatively, the infrared beam may be passed through a multipass gas cell (MPGC) before it reaches the detector (Spellicy and Webb, 2002; Stedman and McLaren, 1996; McLaren and Stedman, 1996). This technique, like ACAMS, is an example of point monitoring, because the contents of the cell are drawn from one specific location. The base path length between the mirrors of the gas

<sup>1</sup>Optical Remote Sensing to Detect and Map Low Levels of Chemical Threat, presentation by Ram A. Hashmonay, Arcadis, to the Technologies for Chemical Agent Detection Workshop, Washington, D.C., August 24, 2004.

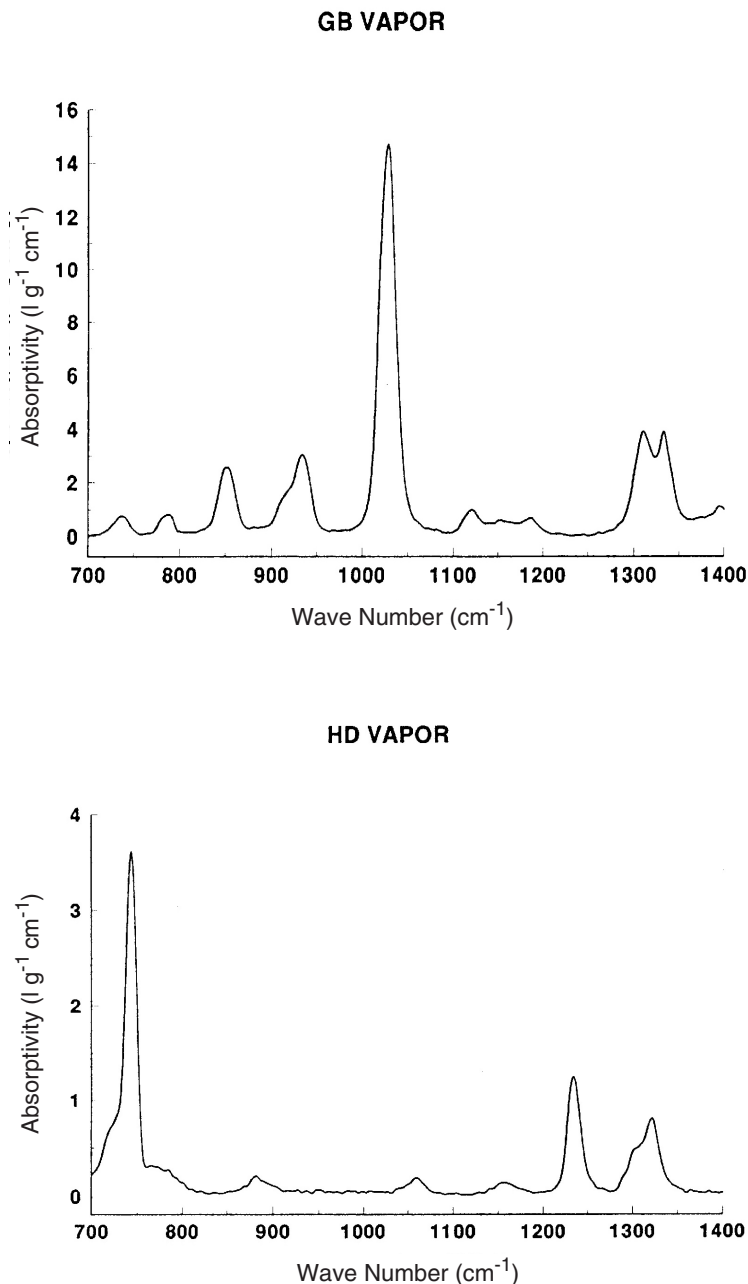


FIGURE 5-1 Infrared spectra of GB vapor (top) and HD vapor (bottom) in the 700 to 1400 cm<sup>-1</sup> region. SOURCE: Courtesy of Scott McLaren, Apogee Scientific, Inc., and Donald Stedman, University of Denver.

cell is typically between 2 m and 10 m, with up to 100 passes. See Box 5-1 for an expansion on detection-limit estimates.

OP/FT-IR measurements have advantages and disadvantages relative to the use of MPGCs. The biggest advantage is that the spectrum changes instantly when a plume of the analyte enters the beam path, whereas with MPGC measurements, the contents of the cell are exchanged relatively slowly. The presence of the analyte anywhere in the beam

path gives rise to an absorption band in the spectrum. Conversely, for MPGC measurements, if the analyte plume is not at the sampling point, it is not picked up. (This is, of course, a disadvantage with any point monitoring technique.) Since the path-integrated concentration is measured in OP/FT-IR measurements, the actual concentration at any point in the plume is never measured directly. For example, if the path length is 400 m and a plume with a concentration

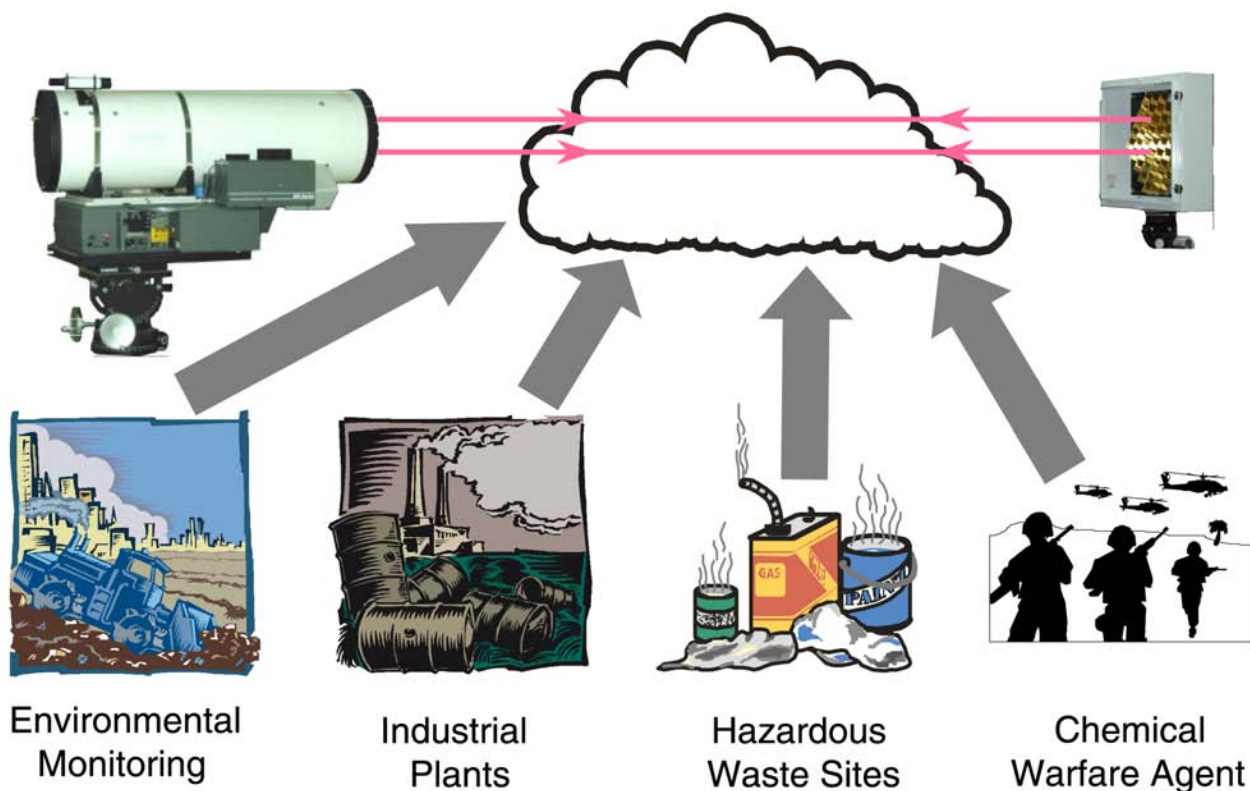


FIGURE 5-2 Schematic depiction of open-path Fourier transform infrared spectroscopy. SOURCE: Courtesy of H. Yang, University of Idaho.

### BOX 5-1 Detection-Limit Estimates for Open-Path FT-IR Spectroscopy

Practical detection limits for OP/FT-IR may be estimated using Equation (5-1a) and the vapor spectra shown in Figure 5-1 of this chapter. The absorbance  $A$  is defined as

$$\log_{10} T = \log_{10} (I/I_0),$$

where  $I_0$  is the incident light intensity and  $I$  is the light transmitted through the optical path. The absorptivity is absorbance divided by path length (in centimeters) times concentration (in grams of analyte per liter). For OP/FT-IR, the minimum detectable absorbance change  $\delta A$  is  $\sim 1$  part in  $10^3$ , with current instrumentation. A practical path length would be 500 m, or  $5 \times 10^4$  cm. From Figure 5-1, the most intense GB vapor absorption band has a peak absorptivity of  $15 \text{ L g}^{-1} \text{ cm}^{-1}$ . Thus, the minimum detectable vapor GB concentration is  $10^{-3}/(15 \text{ L g}^{-1} \text{ cm}^{-1} \times 5 \times 10^4 \text{ cm}) = 1.3 \times 10^{-9} \text{ g/L}$  or (since 1 cubic meter = 1000 L)  $1.3 \times 10^{-6} \text{ g/m}^3$ , that is,  $1.3 \times 10^{-3} \text{ mg/m}^3$ . These detection limits are further degraded by interfering species, moisture, rain, and atmospheric turbulence.

This estimate is to be compared with the 2003/2004 AELs in Table 2-2 in Chapter 2 for GB, which are  $10^{-4} \text{ mg/m}^3$ ,  $3 \times 10^{-5} \text{ mg/m}^3$ , and  $1 \times 10^{-6} \text{ mg/m}^3$  for the STEL, WPL, and GPL, respectively. It is evident that the sensitivity of OP/FT-IR is at best a factor of 13 to 1300 less sensitive than is required for real-time measurement at these levels. It may also be noted that simply measuring the spectrum at the wavelength where the absorptivity is at a maximum cannot account for the effects of interferents, so most workers in OP/FT-IR prefer to measure several weaker bands in the spectrum along with the strongest band. The AELs for HD mustard are higher than those for GB (Table 2-2), but the infrared detection limit is also less favorable because the maximum absorptivity of the bis(2-chloroethyl sulfide) molecule is about a factor of four smaller than that for GB (Figure 5-1). OP/FT-IR might be barely able to detect HD mustard at the STEL, but is a factor of 12 to 250 too insensitive for detection at the WPL and GPL, respectively.

of  $1 \text{ mg/m}^3$  is only present in a 50 m portion of the path, the concentration that would be calculated if it is assumed that the analyte is uniformly distributed over the optical path is  $0.125 \text{ mg/m}^3$ . Thus, the concentration of agent present only in a small segment of the beam path must be very high if the analyte is to be detectable by OP/FT-IR spectroscopy.

A subtle disadvantage of OP/FT-IR spectroscopy is that the sample is at ambient temperature, and hence its absolute temperature can vary by more than  $\pm 20^\circ\text{C}$  depending on the time of day and the season. Conversely, the temperature of MPGCs may be controlled fairly accurately. Compensating for the lines in the vibration-rotation spectrum of water vapor is much easier if the sample is always at the same temperature. Similarly, reference spectra of chemical agents are typically measured at ca.  $20^\circ\text{C}$ . Since the infrared spectra of all vapor-phase species vary slightly with temperature, quantitative errors may result.

Stedman and McLaren (1996) were able to monitor the concentration of GB in a room at the Chemical Agent Munition Disposal System in Utah using a 96-pass MPGC with a base path length of 6.5 m (total path of 624 m). Using a stored background spectrum, they reported a detection limit of  $0.005 \text{ mg/m}^3$ . Absorption by lines in the spectrum of water vapor was the principal source of interference. By employ-

ing a differential technique whereby the previously measured spectrum was used as the background, the detection limit of GB was reduced to  $0.0005 \text{ mg/m}^3$ . However, only changes in the concentration of GB that occur on the time scale of the infrared measurement can be observed with this technique. Thus, it is only useful for detecting catastrophic events in which the concentration of the agent changes very rapidly; it is not likely to be suitable for routine monitoring of agents at the current STELs.

Since lines in the spectrum of water vapor are the main cause of interference, both OP/FT-IR and MPGC approaches would yield poorer detection limits in regions of high humidity (e.g., Anniston, Alabama) than were measured at Tooele in the Utah desert.

McLaren and Stedman (1996) found that detection limits in stack gases increased by at least an order of magnitude because of interference due to the very high partial pressure of water vapor in the stack gases. They also reported that the mirrors in the MPGC became fouled a short time after the flow of the furnace gases was initiated. Single-beam spectra reported by Stedman and McLaren (1996) measured with incinerator exhaust gases (upper trace) and room air (lower trace) flowing through the multipass gas cell are shown in Figure 5-3.

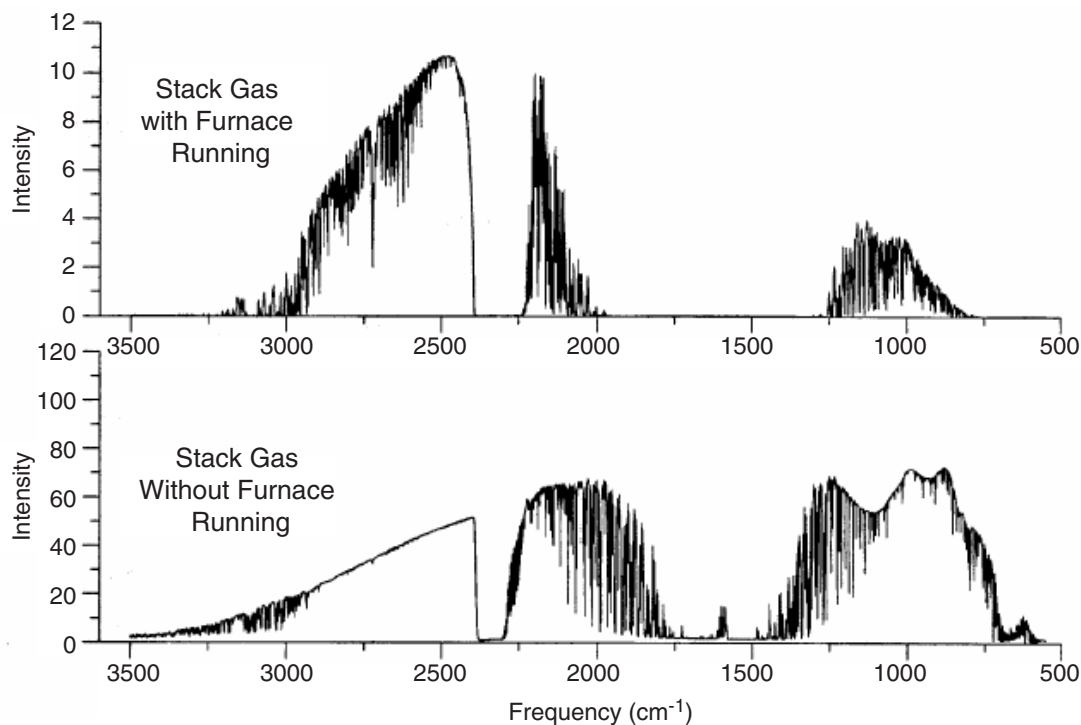


FIGURE 5-3 Single-beam spectra collected when the furnace from which exhaust was being sampled was operating (top) and not operating but drawing ambient facility air (bottom). NOTE: The path length for these spectra was 208 m. Note the 10-fold difference in the ordinate scale and the fact that intense water lines can be seen throughout the entire atmospheric window between about  $1250$  and  $750 \text{ cm}^{-1}$  in the upper spectrum. SOURCE: Stedman and McLaren, 1996.



**Finding 5-1.** In general, the use of FT-IR spectrometry with either open-path or multi-pass gas cell sampling for monitoring chemical warfare agents (CWAs) at levels below about  $0.05 \text{ mg m}^{-3}$  in the atmosphere near the perimeter of chemical agent storage facilities or demilitarization plants is not likely to be effective because of the low sensitivity of this technique. Conversely, FT-IR spectrometry may play an important role in monitoring accidental releases of chemical agents in locations very close to where the agents are stored or incinerated and where the concentration may exceed  $0.05 \text{ mg m}^{-3}$ . Detecting a catastrophic release within a minute of the event would allow suitable action to be taken.

### Surface-Enhanced Raman Scattering

An alternative to absorption-based measurements is based on scattering or re-emission of absorbed light, either as fluorescence or Raman scattering. The measurement of fluorescence from analytes at ppb levels in solution can often be the most sensitive of all quantitative spectroscopic techniques, provided that the molecule of interest has a high quantum efficiency (fluorescence yield) at the analytical wavelength. Unfortunately, most airborne chemical agents do not fluoresce at any easily accessible wavelength and are not present in solution. The UV spectra of the agents are typical of substances that do not possess significant fluorescence yields (Rewick et al., 1986). Not surprisingly, no reports of the successful application of fluorescence for the detection or quantification of airborne chemical agents have been found.

Raman spectrometry exploits the fact that a small portion of the light scattered by a molecule is shifted in frequency by an amount corresponding to a vibrational/rotational transition characteristic of that molecule. While standard Raman spectrometry has nowhere near the sensitivity required to detect very low levels of chemical agents,<sup>2</sup> a variant of Raman spectrometry, known as surface-enhanced Raman scattering (SERS), does. In SERS, analytes are deposited on the roughened surface of one of the coinage metals (Ag, Au, Cu). Under the right conditions, the Raman spectrum can be enhanced by four orders of magnitude. Several companies have been developing ways of automatically sampling a variety of analytes, and a few papers reporting on the detection of chemical agents have been published (Alak and Vo Dihn, 1987; Farquharson et al., 2002). These reports deal with the adsorption of agents onto colloidal SERS probes from water and show typical detection limits of tens of ppb.

<sup>2</sup>Raman cross sections of chemical agents are rather small (6 to  $10 \times 10^{-30} \text{ cm}^2/\text{sr}/\text{molecule}$ ) (Christesen, 1988) and because of their weak UV absorption (Rewick et al., 1986), do not display significant preresonance enhancement. Christesen (1988) concluded that Raman spectroscopy “lacks adequate sensitivity for application to chemical agent remote sensing.”

In a system reported by Sylvia et al. (2000), air containing 2,4-dinitrotoluene was passed over a SERS substrate and measured by Raman spectroscopy with a fiber-optic probe. The detection limit was about 5 picograms of 2,4-DNT. The system and spectra that were measured are shown in Figures 5-4 and 5-5, respectively.

While these results are quite promising, the issue of regenerating the roughened gold sensor was not addressed in Sylvia et al. (2000). It should be noted that (1) the concentrations of 2,4-DNT were in the low ppb range, that is, significantly higher than the target AELs for nerve agents and (2) the Raman cross section of nitro-aromatics is much higher than that of phosphonate esters. Several other objections can also be raised to this approach. First and most important, the time resolution will be poor, probably no better than that of ACAMS—that is, these measurements are near real time, not real time. Second, it is very unlikely that any chemical agent will be present as the lone analyte. For example, the air in the region of wooded areas such as Anniston, Alabama, will be loaded with many terpenes and other volatile organic compounds. It is likely that the SERS signal will be masked by the signals from the interferents present at much higher concentrations. The same argument can, of course, be made about OP/FT-IR measurements.

**Finding 5-2.** Although SERS is the most promising infrared technique of any reviewed by the committee, it is unlikely to be any more sensitive or faster than ACAMS and probably would be less selective and more subject to interference from other airborne molecules.

### OVERVIEW OF ION MOBILITY AND MASS SPECTROMETRIC TECHNIQUES

Mass spectrometry and ion mobility spectrometry (IMS) are both highly sensitive analytical techniques involving ions. The instrumentation comes in many forms, and both types of instruments have been used to detect chemical agents (Hill and Martin, 2002). In mass spectrometry, one detects the chemical of interest by measuring the mass of an ion made after ionizing the molecule of interest, while in ion mobility spectrometry, one detects the time that a pulse of ions traverses through a buffer gas, which is related to its mass. However, the IMS signal’s mass relationship is broad, and therefore the technique is not very selective. Inevitably, mass spectrometers involve vacuum systems and ion mobility spectrometers generally do not. This creates a significant difference in the size and cost of the instrumentation. The lack of a vacuum system in an ion mobility spectrometer makes it more suitable for field deployment.

Mass spectrometers are often referred to as the “universal detector,” because some signal can be obtained from essentially any molecule. Electron impact mass spectrometers involve ionizing the sample after it has already entered into the vacuum region. Frequently, this involves 70 eV electrons,

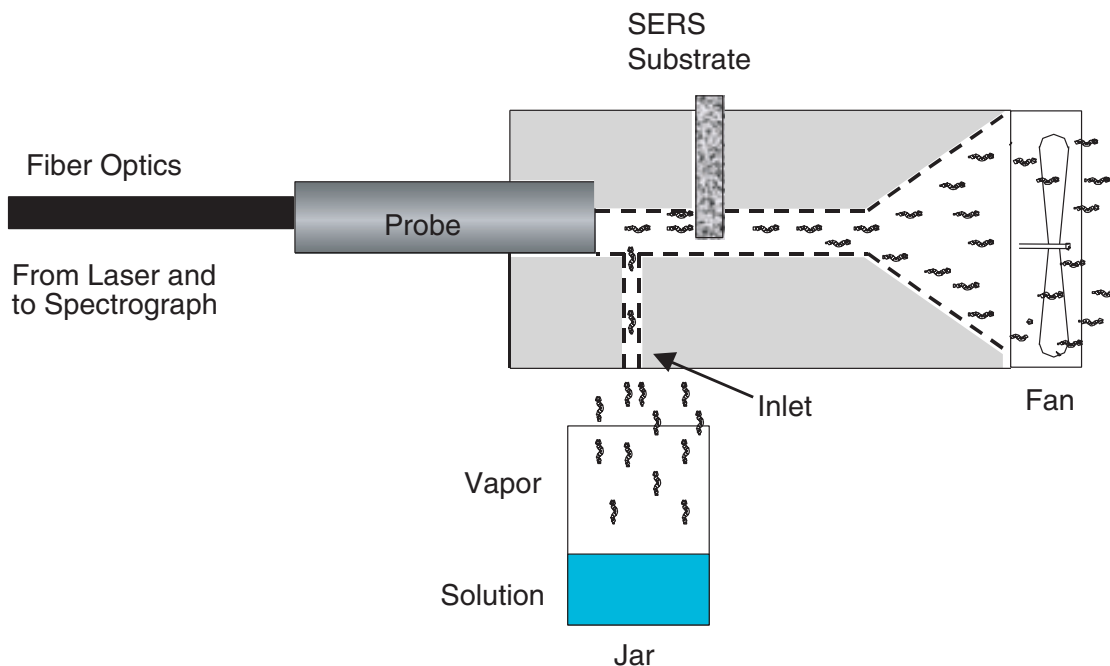


FIGURE 5-4 Schematic diagram of the system used to show the feasibility of surface-enhanced Raman scattering (SERS) measurements of low-concentration explosives in the vapor phase. SOURCE: Reprinted with permission from Sylvia et al., 2000. Copyright 2000 American Chemical Society.

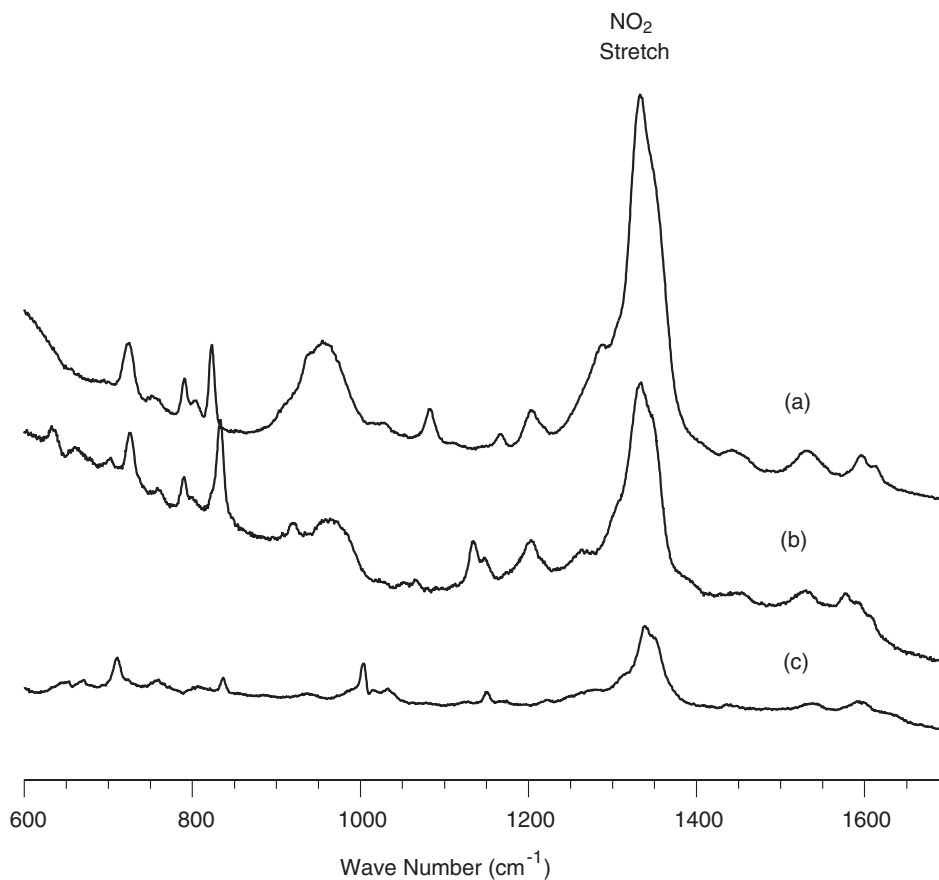


FIGURE 5-5 SERS spectra of (a) 5 pg of TNT, (b) 25 pg of 2,4-DNT, and (c) 50 pg of 1,3-DNB recorded with a 115 mW 785 nm diode laser in 30 s. SOURCE: Reprinted with permission from Sylvia et al., 2000. Copyright 2000 American Chemical Society.

which often leads to fragmentation of the molecule of interest. This fragmentation leads to a loss of selectivity, since a particular mass ion can originate from a molecule having that mass or greater. In order to get both more selectivity and more sensitivity, other ionization schemes are frequently used, including chemical ionization. The latter involves ion-molecule reactions that have exothermicities sufficiently

small that fragmentation frequently does not occur. This leaves the molecule of interest intact, thus providing positive mass identification and leading to an increase in selectivity.

As an example of the difference between the two techniques, the electron impact (EI) and chemical ionization (CI) spectra from  $\text{CH}_3\text{CNH}^+$  of VX are shown in Figure 5-6. While the electron impact spectrum has many peaks, the

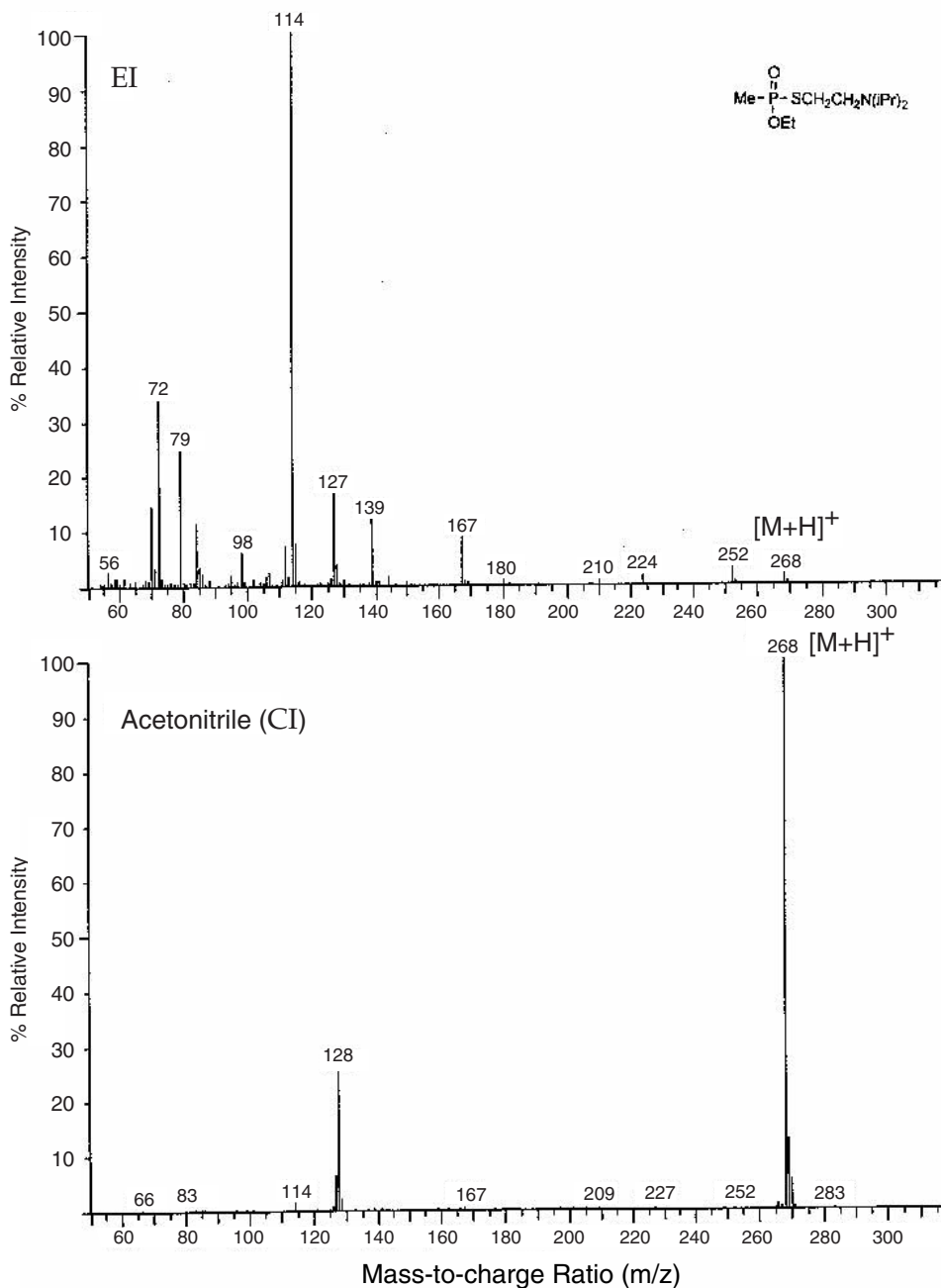


FIGURE 5-6 (Top) Electron impact (EI) and (bottom) acetonitrile chemical ionization (CI) mass spectra of VX agent. The lower trace results from chemical ionization, using  $\text{CH}_3\text{CNH}^+$  as the proton transfer medium. By far the dominant peak is protonated VX, with only one other species at  $m/z = 128$  having significant intensity. SOURCE: Rohrbaugh, 1998.

chemical ionization spectrum is dominated by the parent plus one peak. The sensitivity enhancement is due to the ionization occurring at high pressure where the number density is high. The high-pressure ionization advantage applies to ion mobility spectrometry as well.

Figure 5-7 is a schematic representation of a chemical ionization mass spectrometry (CIMS) instrument. Ions are created at the front end of the instrument in an appropriate ion source. After introduction of the sample, the source ions are allowed to react with the sample in a reaction zone. Finally, the ions are sampled into the mass spectrometer and detected. Sensitivity can be increased by producing more ions or by increasing the reaction time. If depletion of the primary ion does not occur, the technique is linear in response to the target molecule. In an ion mobility spectrometer, the ions are pulsed, then transported by an electric field and collected as an ion current on a grid.

The advantage of ion mobility instruments is that they are less complex and therefore cheaper and easier to run than are mass spectrometers. The big drawback is that false positives are common, because compounds with similar weights and molecular shapes are also detected at approximately the same transit time. Several versions of ion mobility spectrometers are used in the field to detect chemical agents (IOM, 1999; Hill and Martin, 2002). These instruments include the Chemical Agent Monitor, Improved Chemical Agent Monitor, Improved Chemical Agent Point Detector System, and Automatic Chemical Agent Detection Alarm. Several of these are small, hand-held units, and false positives are common. They are able to detect concentrations at the IDLH level in 10 s but are not sensitive enough to detect at the STEL. A new technique uses highly asymmetric electric fields but further increases the complexity (Guevremont, 2004). Since use at chemical demilitarization facilities is not constrained by weight or power requirements, and IMS instruments tend to yield many false positives, they will not be considered further.

To increase selectivity further, second-order mass spectrometry, usually termed mass spectrometry/mass spectrometry (ms/ms), can be performed. In this method, the high-energy ions collide with an inert gas at high energy and fragment.

Different ions at the same mass often lead to unique fragmentation patterns such that this technique can lead to large increases in selectivity. Additionally, the use of mass spectrometers with high resolving power can unambiguously determine the chemical formula, for example, CO and N<sub>2</sub>, each of which has a nominal mass-to-charge ratio,  $m/z = 28$ , but with peaks separated by a small fraction of a mass unit.

Chemical ionization mass spectrometers use ionization by chemical reaction. Frequently, proton or charge (electron) transfer is used. These instruments can be both extremely sensitive and selective if the proper ion is used in the source. Several studies involving chemical ionization mass spectrometers to detect chemical agents have been reported, all utilizing positive ions (D'Agostino and Provost, 1986; Rohrbaugh, 1995, 1998, 1999, 2000).

Chemical ionization mass spectrometers have been used for many years. Those currently in use in atmospheric chemistry represent a new generation of instrumentation and serve as a guide for sensitivities and selectivities that are currently possible. The atmospheric instruments are both custom built and commercially available, although the latter are not as sensitive as the former. Many of them are used on airplanes and need to be compact. Additionally, some of the airplane platforms have only pilots aboard and therefore require totally automated instrument operation. The automation includes not only the actual measurements but calibrations and subtractions for background species. These instruments are programmed to run at least as long as an airplane flight without user attention. Extending such instrumentation to continuous, autonomous operation is straightforward and would only require ensuring a continuous gas supply for the ionization flow reactor. Instruments used for atmospheric studies require the ability to sample at numerous altitudes and with wind speeds equal to the aircraft speed. These are harsh conditions. The ability of the atmospheric instruments to operate remotely and under a range of stressing conditions should mean that the technology could be adapted for the long periods of reliable operation necessary for use at chemical demilitarization facilities.

A commercial instrument now used extensively by the atmospheric studies community is made by Ionicon Analytik

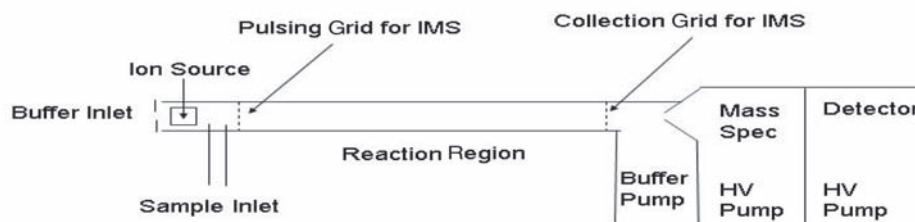


FIGURE 5-7 Schematic diagram of a generic chemical ionization mass spectrometry (CIMS) instrument. NOTE: IMS, ion mobility spectrometry; HV, high volume. SOURCE: Courtesy of committee member A. Viggiano, Air Force Research Laboratory.

in Austria.<sup>3</sup> In this instrument,  $\text{H}_3\text{O}^+$  ions are made in a hollow cathode discharge source, which is extremely stable. The  $\text{H}_3\text{O}^+$  ions are injected into a drift tube, where they are declustered and allowed to react with trace constituents, mainly by proton transfer. The resulting ions are detected by a quadrupole mass spectrometer. This requires that the proton affinity of the molecule of interest be higher than that of water, in order to ensure that the reaction is exothermic. Work has been done on proton transfer to chemical agents from  $\text{CH}_5^+$  (Rohrbaugh, 2000);  $\text{HCH}_3\text{CN}^+$  (Rohrbaugh, 1998);  $\text{NH}_4^+$  (Rohrbaugh, 1995; D'Agostino and Provost, 1986); and  $\text{CH}_3\text{OH}_2^+$  (Rohrbaugh, 1999). The latter ion was shown to produce little fragmentation. Both proton transfer and clustering were commonly observed with  $\text{NH}_4^+$ , and were described as both sensitive and selective. These studies show that protonated species enable sensitive detection of the relevant chemical agents and their degradation products. It should be possible to produce such ions in the Ionicon source by introduction of small amounts of the hydrogen-containing analytes.

The sensitivity of the Ionicon instrument is approximately 0.1 cts/s/ppt, where cts is an abbreviation for counts (de Gouw et al., 2003). Therefore, if the chemistry is clean—that is, there is no background or interference—an accurate measurement of 1 ppt can be made in several minutes. However, interferences at this level are common, since many molecules have proton affinities greater than that of water. Common sensitivities for various chemicals are typically in the tens to hundreds of ppt. Comparing with the IDLH values of 16,000 ppt, 250 ppt, and 100,000 ppt for GB, VX, and HD, respectively, this instrument has the capability to measure these levels in less than 1 s. Measurements at the STEL should be difficult except for HD (423 ppt). A version of the instrument that uses an ion trap mass spectrometer is under development, and this should help in ion identification by reducing interferences, enabling ms/ms measurements to be made.

The custom-built instruments for atmospheric chemistry have much better sensitivity and use a variety of ions as the chemical ionization medium. Generally, these instruments use either proton transfer from  $\text{H}_3\text{O}^+$  or a variety of negative ions as the precursor ionization species. The use of negative ions has not previously been explored for use in detecting chemical agents, although it was speculated in a past report that negative ions would be suitable, since there should be no background problem from hydrocarbon interference (Ketkar et al., 1989).

The most sensitive custom-built instrument is the National Center for Atmospheric Research (in Boulder, Colorado) instrument for sulfuric acid vapor detection, in part because

there is essentially no background (Eisele and Tanner, 1993). This instrument uses a radioactive ion source that is extremely stable and reliable to make  $\text{NO}_3^-$  as the precursor ionization species, and it offers an impressive sensitivity of 1000 cts/s/ppt. This translates into 1, 10, and 60 s detection limits of 0.003, 0.001, and 0.0003 ppt, respectively. This instrument is rather large—it takes up two aircraft racks and weighs 400 lb. A version half as sensitive but half this size, achieved mainly through the use of smaller pumps, is under construction.  $\text{NO}_3^-$  would not be expected to react with chemical agents, but it may form cluster ions with the agent molecules. Substitution of another ion such as a proton transfer agent should be straightforward. These extremely low detection limits are such that even the GPL of VX (0.05 ppt) could be detected in 1 s. Of course, this relies on finding a suitable chemical ionization species. An instrument at the Georgia Institute of Technology that uses similar chemistry is a factor of three less sensitive and is fully enclosed in a wing pod on the aircraft (Chen et al., 2005). The sensitivity of this instrument is still high enough to be able to detect a compound at the GPL limit of VX.

A different approach is being taken by a group at the National Oceanic and Atmospheric Administration (NOAA) in Boulder, Colorado (Marcy et al., 2005). Various  $\text{F}^-$  transfer agents are used as the CI medium, including  $\text{SF}_5^-$ ,  $\text{SF}_6^-$ ,  $\text{SiF}_5^-$ , and  $\text{CF}_3\text{O}^-$ . The instrument uses a beta emitter that is sold as an in-line ionizer (i.e., it does not need a permit). For a variety of compounds, the sensitivity is a few counts per second per ppt, with detection limits on the order of 1 to 30 ppt in 1 s. This is good enough so that it may be possible to allow the STEL for GA/GB (16 ppt) and VX (0.84 ppt) to be detected in real time (1 to 10 s). The AEL limits for HD are much larger than those for the nerve agents, so it may be possible to detect HD at the GPL with a suitable CIMS instrument in real time. Since ion molecule reactions are generally fast when exothermic, it will be worthwhile to use *ab initio* calculations to determine  $\text{F}^-$  affinities for the chemical agents. If exothermic,  $\text{F}^-$  should be very sensitive and most likely background free, since the molecular weights of the chemical agents are relatively high. Several  $\text{F}^-$  transfer agents are easily made, and the chemistry should easily be transferable to the more sensitive instruments described above.

Two groups (Air Force Research Laboratory (AFRL), Hanscom Air Force Base; and Max Planck Institute (MPI), Heidelberg, Germany) use  $\text{CO}_3^-$  as the chemical ionization species. The sensitivity for the AFRL instrument is about 5 cts/s/ppt (Ballenthin et al., 2003), about the same as for the NOAA instrument. The MPI instrument sensitivity is similar. The  $\text{CO}_3^-$  is made in a corona discharge, which is another stable, reliable ion source.  $\text{CO}_3^-$  may be a good precursor ionization species if the  $\text{F}^-$  transfer agents noted above do not work, since it tends to be quite reactive, often transferring an O atom. For example, preliminary experiments

<sup>3</sup>Additional information is available online at <http://www.ptrms.com>. Last accessed July 25, 2005.



show that it is sensitive to TNT.<sup>4</sup> One detriment is that detection with  $\text{CO}_3^-$  tends to be sensitive to water vapor. This sensitivity would vanish in the Ionicon instrument. The Heidelberg instrument also uses  $\text{NO}_3^-(\text{HNO}_3)$  and  $\text{H}_3\text{O}^+$  as chemical ionization species. The most recent version of the MPI instrument uses a quadrupole ion trap as the mass spectrometer. The main advantage of doing so is that collision-induced dissociation experiments can be performed to aid ion identification.

The preceding discussion shows that current state-of-the-art CIMS instrumentation can readily detect certain chemical species at concentrations well below the IDLH limit in real time, that is, 1 s. Real-time detection at the STEL is also likely for several agents. The best instrumentation should be able to detect concentrations for the most stringent monitoring requirement, that is, the GPL of VX, in real time. The problem is in choosing a source ion that is both sensitive and selective. Negative ions hold much promise mainly in terms of selectivity and therefore small background. The ion chemistry is relatively easy to test, both through calculations and through the use of surrogates in ion-molecule reactors such as flow tubes and ion cyclotron resonance instruments. It should be possible to accomplish these feasibility studies in a few months.

A recent development in mass spectrometry related to the detection of surface contamination deserves mention. The Cooks group at Purdue University has recently invented a new technique called desorption electrospray ionization (DESI) (Takats et al., 2004). In this approach, an electrospray source is aimed at a surface, and the ions formed are sampled into an ion trap mass spectrometer through an ion transfer line. The Cooks group has been able to observe the chemical warfare agent simulant dimethyl methylphosphonate (DMMP) on nitrile gloves exposed to DMMP for only 1 s. This was accomplished even after the gloves were washed and dried. The low-volatility explosive cyclotrimethylenetrinitramine (RDX) was also detected on a leather surface. A similar plasma entrainment/ionization technique termed Direct Analysis in Real-Time (DART) has been developed by JEOL USA, Inc. DART has also been used to entrain and ionize a wide variety of chemicals adsorbed on surfaces, including VX for most spectrometric analysis (Cody et al., 2005). The DESI and DART techniques, which seem easy to use, show great promise as a means for determining whether materials that may have been exposed to chemical agents are contaminated.

**Finding 5-3.** Chemical ionization mass spectrometry (CIMS) is a highly sensitive technique that may be able to

detect all chemical agents in real time, potentially even at the general population limit. Previous work has focused exclusively on positive ion precursors. Instruments in the atmospheric community extensively use negative ions as a precursor, leading to increased selectivity without sacrificing sensitivity. Commercial CIMS instruments are already available, although with reduced sensitivity.

**Recommendation 5-3.** The Army should investigate whether present CIMS instrumentation could be immediately used to detect chemical agents at the IDLH limit in real time. The use of negative ions as a precursor should be investigated to improve selectivity. Adaptation of one of the research-grade atmospheric field instruments for real-time detection between the STEL and the GPL for each relevant agent should be considered.

## MOLECULAR-LEVEL CHEMICAL SENSORS

A number of innovative technologies exist that have the potential for contributing to the chemical agent monitoring effort. Significant developments are occurring in the area of molecular chemical sensors. These technologies may be able to provide new or supplementary means for worker monitoring, or they may provide the capability for networked sensing outside the fence line of incineration facilities. These methods rely on new sensing paradigms and new chemistries.

Conventional analytical measurements often involve three distinct steps: sampling, pretreatment, and measurement. First, a representative sample is collected. This often entails preconcentrating the sample by passing large volumes of air or water through a filter or adsorbent. Second, to remove interfering substances, the sample is processed by such techniques as chromatography, precipitation, and distillation. In some cases, a label (e.g., dye or electroactive label) is attached to the analyte to make it detectable. Finally, an actual measurement is made on the processed sample.

Chemical sensors integrate all three of these operations. The sampling often consists simply of exposing the sensor to air containing the analyte, and no preprocessing is needed because all the necessary chemistry to impart selectivity and sensitivity is located within the sensing layer. Thus, molecular-level chemical sensors offer significant simplification, and their response times can be rapid. Because of their design, such sensors make measurements continuously.

The chemical sensing technologies discussed below have all been tested with chemical agents or agent simulants and represent the application of state-of-the-art microsensors and microfluidics to chemical agent detection. In addition to the sensors themselves, significant effort is being directed to developing new sensing materials with the requisite specificity and sensitivity to solve challenging detection problems.

<sup>4</sup>Personal communication between Frank Arnold, senior research scientist, Max Planck Institute for Nuclear Physics, and Albert Viggiano, committee member, November 2005.

### Electronic or Artificial Noses

An emerging approach to broadband chemical detection is inspired by the biological olfactory system (Buck and Axel, 1991; Buck, 1996). These systems are based on using an array of semiselective cross-reactive sensors that produce a response pattern which is characteristic of a particular compound or mixture (Gardner and Bartlett, 1999; Albert et al., 2000). The response pattern is used to “train” a computational pattern-recognition system that “memorizes” the pattern and recalls the identity of the analyte upon subsequent exposure. The combination of array detection, complex pattern generation, and computational processing is similar to the way that the olfactory system performs odor recognition.

#### Conducting Sensor Films

A very large scale integrated circuit (VLSI)-compatible, versatile, low-cost, electronic “nose-chip,” developed at the

California Institute of Technology, has enabled arrays of simple, readily fabricated, chemically sensitive resistor films to be produced. An array of sensors that individually respond to vapors can produce a distinguishable response pattern for each separate type of analyte or mixture. Pattern-recognition algorithms and/or neural network hardware are used on the output signals from the electronic nose to classify, identify, and, where necessary, quantify the vapor or odors of concern.

The underlying principle of the “Caltech electronic nose” is extraordinarily simple. When a sorption sensor film is exposed to a gaseous vapor, some of the vapor partitions into the film and causes the film to swell (Figure 5-8). This swelling is probed electrically, because each sensor film consists of a composite that contains conducting particles that have been dispersed into a swellable organic insulator. The composites can either be two-phase systems, consisting of a mixture of conductive particles within an insulating, swellable organic polymer, or they can be single-component composites of nanoparticles in which the sorbent phase is covalently

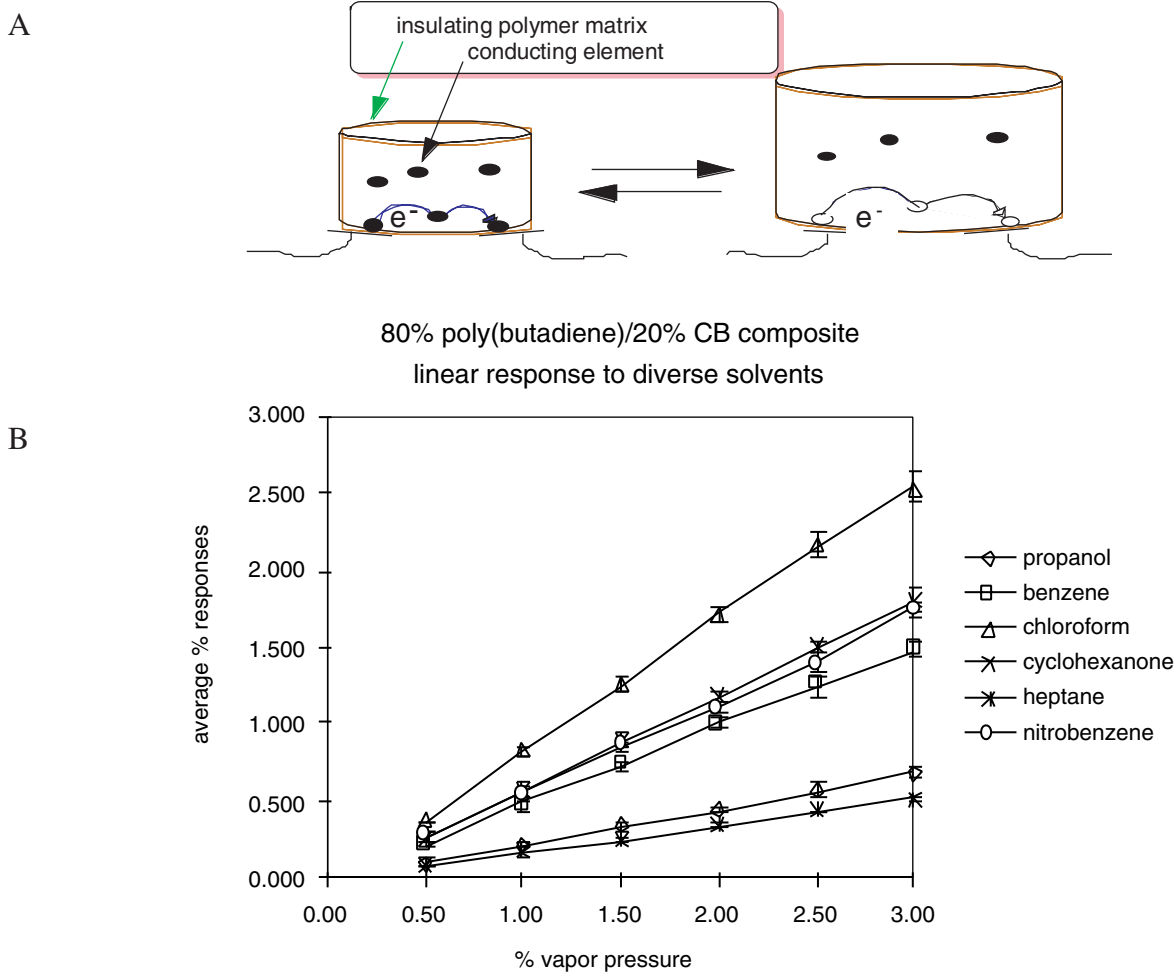


FIGURE 5-8 (A) Swelling occurs as an odorant partitions into the sorption phase. (B) A linear response of an individual sensor signal as a function of concentration is observed for a variety of analytes. SOURCE: Courtesy of N. Lewis, California Institute of Technology.



linked to the nanoparticle through prior chemical reactions (Freund and Lewis, 1995; Lonergan et al., 1996; Doleman et al., 1998; Sotzing et al., 2000). The vapor-induced film swelling produces an increase in the electrical resistance of the film, because the swelling decreases the number of connected pathways of the conducting component of the composite material. Any individual sensor film responds to a variety of vapors, because numerous chemicals will partition into the polymer and cause it to swell to varying degrees. An array of sensors containing different sorption phases yields a distinct fingerprint for each combination of vapors, because the swelling properties over the entire array are different for different vapors (Albert et al., 2000).

The pattern of resistance changes on the array of sensors is diagnostic of the vapor, while the amplitude of the patterns indicates the concentration of the vapor (Severin et al., 2000). Figure 5-9 provides an example of the different patterns produced by various vapors on the electronic nose. Each different odor or analyte produces a different response pattern on an array of such detectors, therefore allowing identification and classification of the target odors through the use of automatic target-recognition techniques (Severin et al., 2000). The swelling/deswelling process is highly reversible in thin polymer films, so typically thousands of cycles can be performed without significant loss of sensor responsivity.

This electronic nose approach to broadband chemical detection has been shown to produce responses in the mid-ppb range to nerve agent simulants DMMP and DIMP either in air or in the presence of much higher concentrations of common interferents such as diesel fuel, lighter fluid, THF, water vapor, and other common solvents (Hopkins and Lewis, 2001). Live-agent testing at the Edgewood Research, Development, and Engineering Center at Aberdeen Proving Ground, Maryland, has shown responses in the low ppb levels for G-class chemical agents. Further improvements in sensitivity are reasonable to expect as the sorbent phase is tailored to be complementary to the chemical properties of the agents of interest (Briglin et al., 2001, 2002). See Figure 5-10.

### *Optical Sensor Arrays*

Tufts University researchers are developing optical sensor arrays. These arrays are prepared by first etching an array of optical fibers. Etching causes wells to form at the end of each optical fiber in the array. The sensors are prepared by attaching fluorescent dyes to microspheres made from various types of commercially available 3 to 5 mm diameter polymer and silica beads or from polymer-coated silica beads (White et al., 1996; Dickinson et al., 1996, 1998, 1999; Albert and Walt, 2000, 2003). Solvatochromic fluorescent indicators (dyes that change their fluorescence according to the polarity of their environment) are incorporated into the beads by entrapment or adsorption. Each dyed bead type represents a stock of  $\sim 1.0 \times 10^{11}$  identically responding bead sensors per gram of material. These sensor stocks can be

combined to form a sensor library suited for vapor detection. A sensor array is fabricated by randomly dispersing the sensor bead library into the etched walls on the face of the optical fiber array (Figure 5-11) (Michael et al., 1998). The size of the beads matches the size of the wells such that only one bead assembles into each well. This dispersion of sensors in a random fashion simplifies array fabrication by eliminating the difficulty of positioning each sensor on a defined point within the array. Hundreds to thousands of each type of sensing bead are represented on the array.

A fluorescence imaging system using a charge-coupled device (CCD) detector is used to monitor sensor array responses. Vapor samples are delivered to the array in a pulsatile fashion via a vacuum-controlled sparging apparatus. The CCD camera records the fluorescence responses for all sensor elements during the vapor pulse. By monitoring each sensor's temporal fluorescence change at a specific wavelength, unique response patterns are collected. The responses are based on how the polarity of the vapor interacts with the sensor bead composition and affects the dye's emission properties.

As described below, the Tufts University optical nose has addressed one of the most challenging aspects of electronic noses—the requirement for extensive “training,” that is, calibration of the response to a specific type and amount of analyte. During training, cross-reactive arrays are exposed to vapors and the responses from the various sensor types are collected and stored in a database. The responses are used to develop a pattern-recognition algorithm, also called a classifier, for all the vapors. Under optimal conditions, these algorithms are able to differentiate one vapor from another, thereby enabling vapor identification upon subsequent exposure. For various reasons, all sensors in all of the different types of arrays discussed in this subsection on electronic or artificial noses will degrade, requiring that sensor arrays be periodically replaced. To date, no two arrays are the same; consequently, every cross-reactive array to date has required its own training because the responses from one array do not transfer to any other array. This need to replace arrays has reduced the enthusiasm for electronic noses because of the need to train every array. The Tufts University optical nose has demonstrated the ability to transfer training from one array to replicate arrays, because the library of microsphere sensors is made in batches and can be used to prepare many identical arrays. As can be seen in Figure 5-12, the data produced by these bead sensors are highly complex in shape, providing high information content that is useful for selectivity.

The Tufts researchers have also developed a sensor array that is sensitive to chemical agents. The array contains both nonspecific sensors that give it broadband sensitivity and a specific sensor type that responds only to reactive compounds, for example, nerve agents and alkylating agents such as HD. This array has undergone testing with chemical agent simulants.

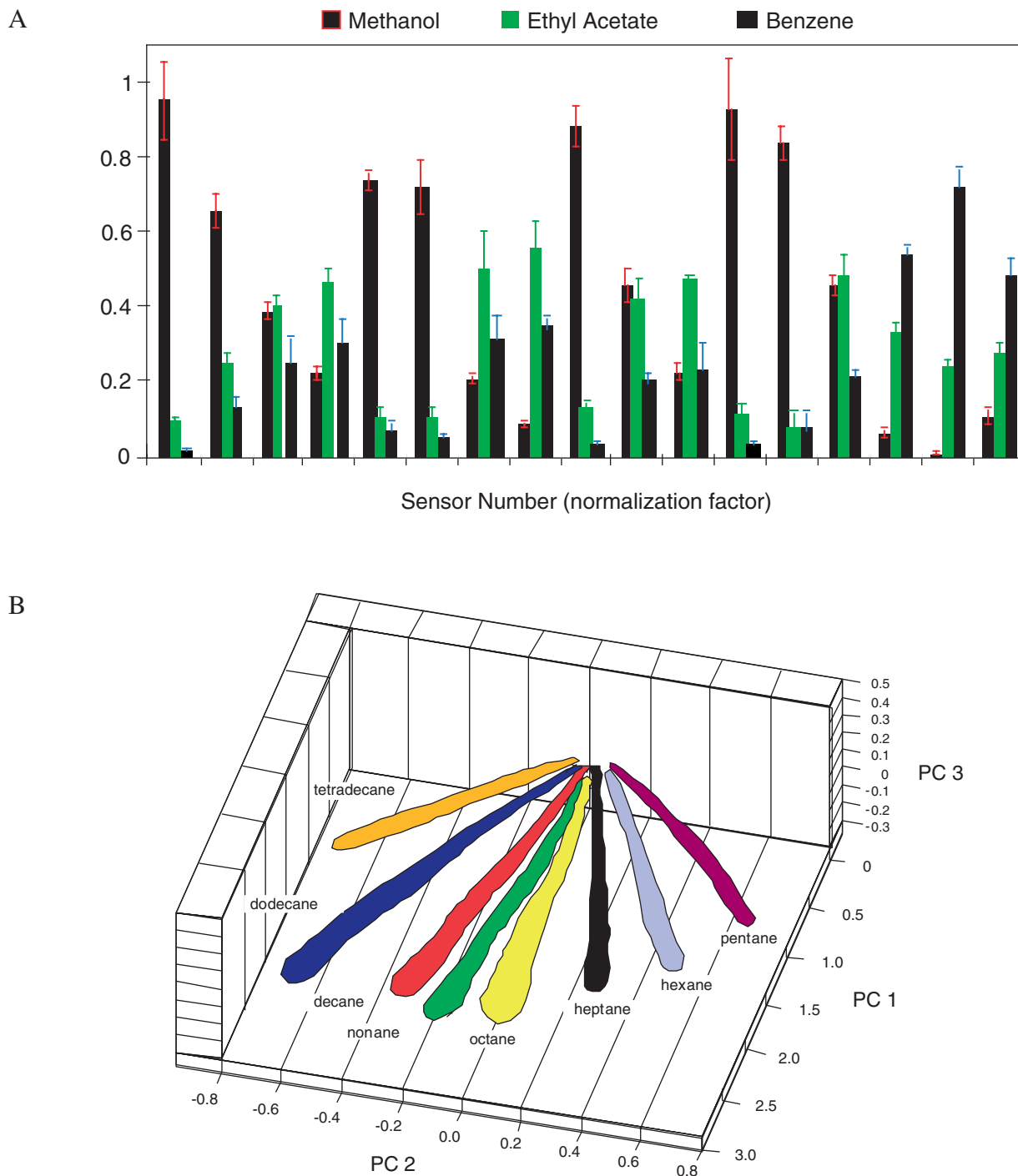


FIGURE 5-9 (A) Response patterns for three different solvents on a 17-element sensor array. (B) Data in principal component space from a 20-detector array exposed to n-tetradecane, n-dodecane, n-decane, n-nonane, n-octane, and n-heptane each at  $P/P^\circ = 0.005$  to  $0.03$  in air (with  $P^\circ$  being the vapor pressure of the analyte at 300 K), showing that the pattern type identifies the vapor, and the magnitude of the pattern signals is linearly proportional to the analyte concentration. Axes labeled PC 1, PC 2, and PC 3 correspond to the first three principal components for the data. SOURCE: Courtesy of N. Lewis, California Institute of Technology.

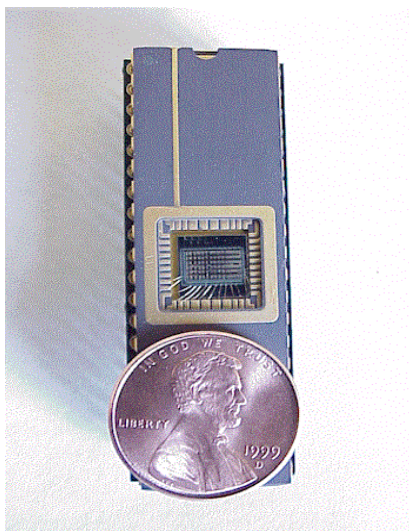


FIGURE 5-10 Photograph of a “nose-chip,” with 12 columns and 6 rows, each having a different polymeric sensor combination and each pixel having a switch under its pair of contact lines. A single printout provides the output of the sensor pixel being interrogated using a row/column addressing scheme. SOURCE: Courtesy of N. Lewis, California Institute of Technology.

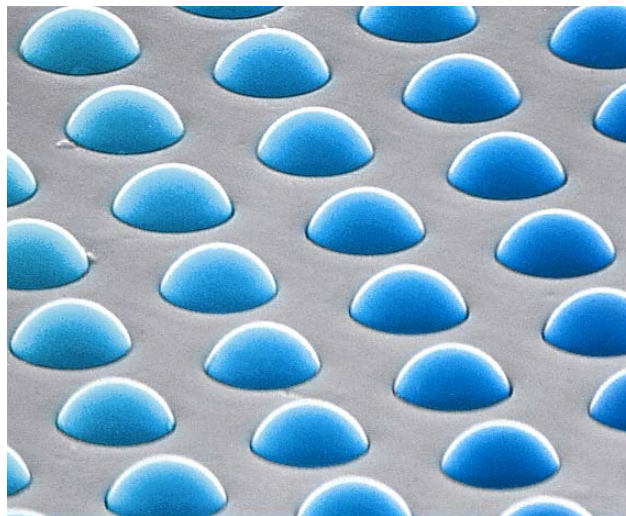


FIGURE 5-11 Microsphere sensors loaded onto the end of an optical fiber array. By averaging the signals of multiple copies of each sensor type in the array, slight differences between beads are eliminated. Furthermore, averaging beads of each sensor type leads to enhanced signal-to-noise ratios. SOURCE: Courtesy of Illumina, Inc.

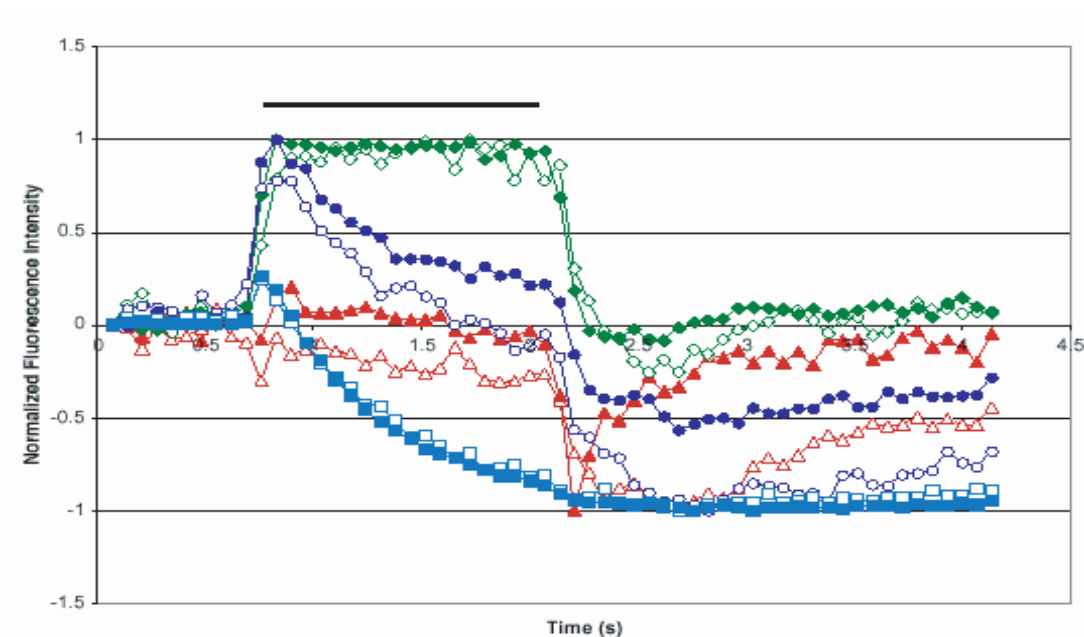


FIGURE 5-12 The average fluorescence response patterns of 12 bead sensors. Benzene (red triangle), toluene (green diamond), 1,3-DNB (●), and 4-NT (■) vapor responses are shown, demonstrating how structurally similar compounds can be distinguished on the basis of differences in their temporal response profiles. The solid black line indicates the time frames during which the vapor pulse (lasting 1.37 s) was delivered to the array. SOURCE: Courtesy of committee member D. Walt, Tufts University.

The Tufts researchers have demonstrated the first artificial nose able to transfer a classifier between two sensor arrays (Stitzel et al., 2001). For commercial applications, transferable classifiers are more efficient because they allow sensor arrays to be replaced without retraining or recalibrating. More importantly, the ability to interchange sensor arrays allows a library of vapor response patterns to be generated, serving as a reference for learned vapors and representing an “odor memory.” This advance could facilitate the investigation of complex problems such as environmental monitoring or clinical diagnostics in which large training sets may be required. Problems of this type are especially difficult because they involve complex mixtures and unknown components that vary from environment to environment or from person to person. A training process alone could be quite extensive and time consuming, requiring hundreds or even thousands of observations to be collected in order to accurately train the array to detect chemical agents in environments with complex backgrounds.

Another type of optical array platform is being developed by the Suslick group at the University of Illinois (Suslick, 2004; Suslick et al., 2004). In this array, a diverse set of chemical indicators, including metalloporphyrins, pH-sensitive dyes, and solvatochromic indicators, are used to generate color patterns that can be read by a color camera and converted into red-green-blue color values for processing (Rakow and Suslick, 2000; Sen and Suslick, 2000). This colorimetric-array sensor technology is based on strong and relatively specific interactions between the analytes and a set of chemoresponsive dyes. The materials cost of the printed arrays is a few cents (the majority of that is the cost of the polyvinylidene fluoride membrane, which in bulk sells for ~\$0.04/cm<sup>2</sup>, and the imaging system is extremely inexpensive (white LED with web camera CCD or even an ordi-

nary flatbed scanner). The arrays have been tested with chemical agents, and the responses to various agents are shown in Figure 5-13. In preliminary studies done in conjunction with ChemSensing (which is commercializing Suslick’s technology) and the Battelle Memorial Institute, excellent sensitivity to several chemical agents was observed, with visual changes in color even at the low ppb level.

### New Materials

Another emerging trend is in the development of new sensing materials.

#### Fluorescent Indicator Detectors

The Swager group at the Massachusetts Institute of Technology has developed a fluorescent indicator that is selective for molecular functional groups. The indicator displays a strong increase in fluorescence in the presence of electrophilic phosphates (Zhang and Swager, 2003). The indicator has differential reactivity to nerve agents (G-agents) relative to the less reactive pesticides, and because it generates fluorescence from a dark state, ultratrace detection of most G-agents is possible. This general method is undergoing further chemical and instrument development by Nomadics, Inc., and working sensor prototypes have been produced that approximate the size of a typical TV/VCR remote (see Figure 5-14). The system gives a reversible response because activated chromophores are readily photobleached, which brings the system back to a stable baseline. Illumination with light removes the color from the activated indicators, thereby returning the signal to baseline. A similar process results in the fading that occurs when a dyed article of clothing is left out in bright sunshine.

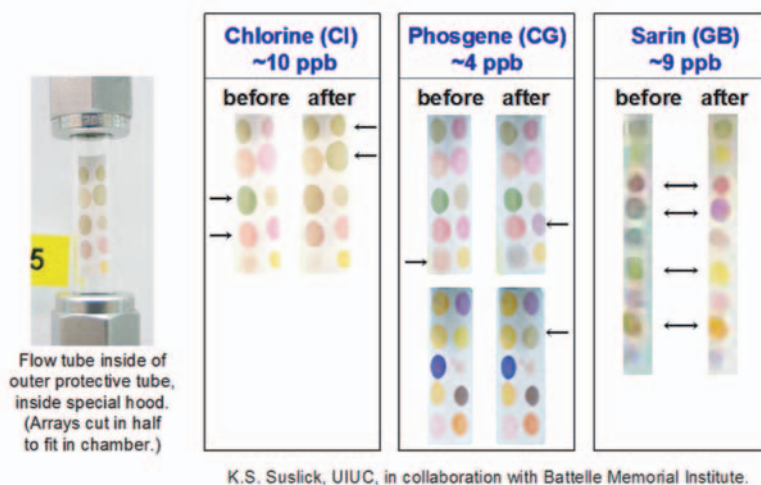


FIGURE 5-13 Color patterns obtained upon exposure to various chemical agents. SOURCE: Courtesy of K.S. Suslick and M.E. Kosal, University of Illinois at Urbana-Champaign.



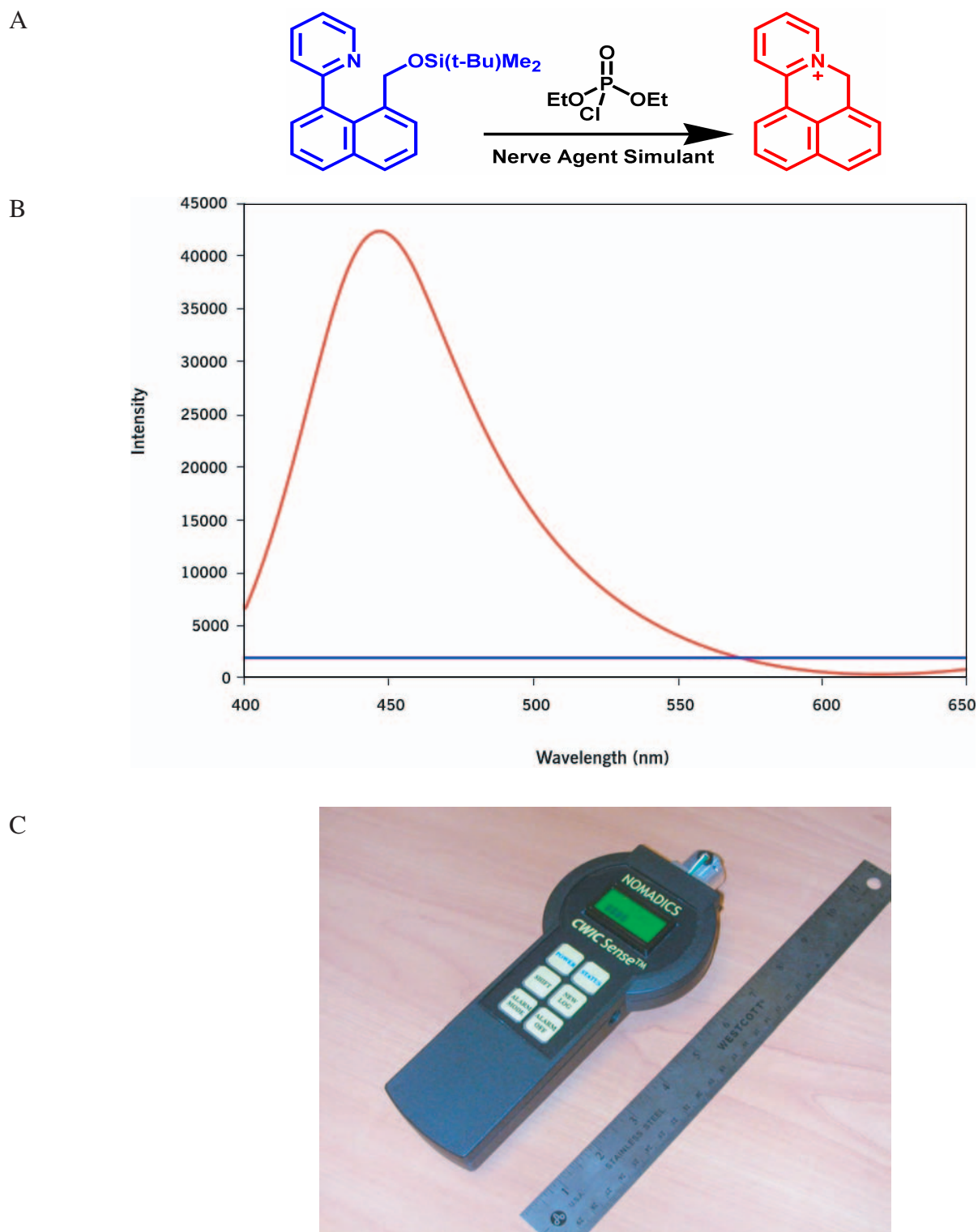


FIGURE 5-14 (A) Reaction of the Chemical Warfare Indicating Chromophore (CWIC) reporter (blue) with a nerve agent simulant produces a fluorescent reporter molecule (red). (B) The fluorescence spectrum of the CWIC before (blue) and after (red) exposure to a nerve agent simulant shows a dramatic increase in intensity. (C) Nomadics, Inc.'s prototype handheld system for chemical detection using the CWIC. SOURCE: Parts A and B: Frye-Mason et al., 2004. Part C: Courtesy of Nomadics, Inc.

The sensitivity of the Nomadics CWIC sensor (Figure 5-14) exceeds the present Department of Defense specifications for the Joint Chemical Agent Detector (JCAD). The CWIC sensor provides a signal-to-noise ratio of 3600 for a 2 second challenge at 0.1 mg/m<sup>3</sup>. This sensitivity can be compared with JCAD specifications requiring the detection of 1 mg/m<sup>3</sup> for <10 s and 0.1 mg/m<sup>3</sup> for <30 s. Recent live-agent testing has indicated that the CWIC detection technology can give comparable detection limits of live agents including sarin, tabun, and lewisite (Frye-Mason et al., 2004).

### Surface-Enhanced Raman Biosensing

Structured nanomaterials for surface-enhanced Raman-based biosensing are being developed by the Van Duyne group at Northwestern University. In this approach, local fields generated by the structured nanoparticles provide a significant enhancement resulting in high-sensitivity measurements using both Raman (Yonzon et al., 2004; Shafer-Peltier et al., 2003) and surface plasmon resonance mechanisms (Haes and Van Duyne, 2002; Riboh et al., 2003; Haes et al., 2004a, 2004b, 2004c) (see Figure 5-15). The ability to enhance the field by creating nanoscale structures opens up the possibility for preparing sensors and sensing materials with high functionality in a small package without sacrificing sensitivity. Furthermore, these new types of materials may provide completely new transduction mechanisms that could be employed for sensing.

### Porous Silicon Technology

The first chemical sensor that utilized the passive optical properties of porous silicon (Si) involved Fabry-Pérot interference from a thin layer (Curtis et al., 1993). The sensing principle of the single-layer Fabry-Pérot films, as well as more complex photonic crystals, is based on what is commonly called the optical thickness of the film. Optical thickness is the product of the refractive index ( $n$ ) and the thickness ( $L$ ) of the film. The electrochemical parameters used in the synthesis of porous silicon control both of these parameters precisely and reproducibly: the current density usually controls porosity and hence  $n$ , and the length of time that the sample is etched determines  $L$ . A high-quality Fabry-Pérot film made of porous silicon has two planar and parallel interfaces and displays high-fidelity fringes in the reflectivity spectrum (see Figure 5-16). A spectral shift in these fringes occurs when the refractive index of the film changes—for example, when a molecule is admitted into the pores—corresponding to a change in optical thickness (Lin et al., 1997). Of the several electrical and optical transduction modes available to porous silicon films, this optical interference method is perhaps the most extensively developed and possibly the most robust. Detection of toxic chemicals (Létant and Sailor, 2000; Sohn et al., 2000), volatile organic compounds (Lauerhaas et al., 1992; Snow et al., 1999; Zangoie et al., 1999), polycyclic aromatic hydrocarbons (Song and Sailor, 1997), explosives (Content et al., 2000; Sailor et al., 2001), DNA (Lin et al., 1997; Chan et al., 2000),

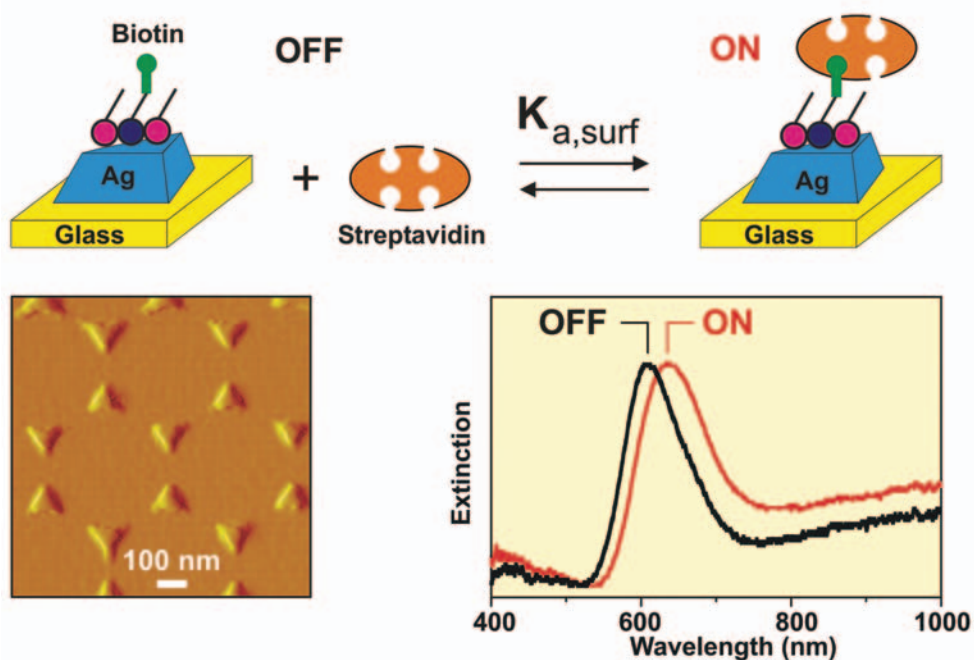


FIGURE 5-15 A nanoscale optical biosensor. Nanoparticle structured surfaces provide field enhancements for chemical detection. SOURCE: Reprinted with permission from Haes and Van Duyne, 2002. Copyright 2002 American Chemical Society.

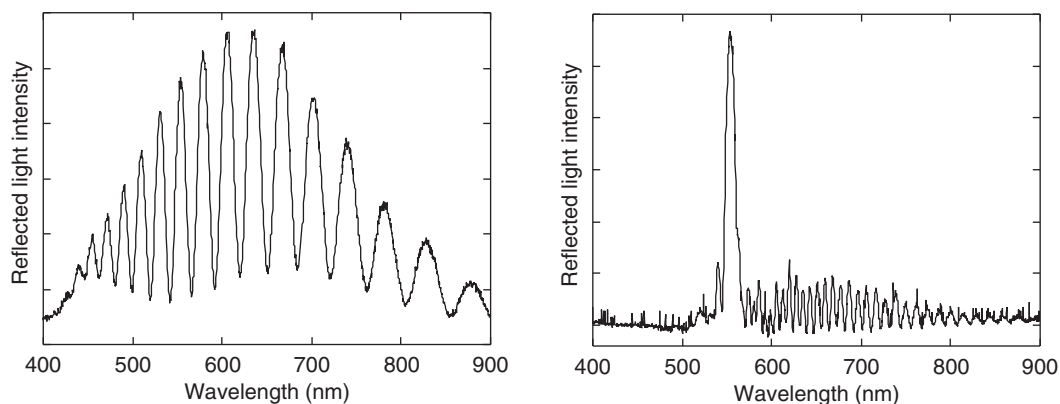


FIGURE 5-16 Reflectivity spectra from a single-layer porous Si film (left) and from a multilayered (rugate filter) porous Si film (right). SOURCE: Courtesy of M.J. Sailor, University of California, San Diego.

and proteins have all been reported (Dancil et al., 1999; Janshoff et al., 1998; Zangoie et al., 1998), and detection limits of at least a few ppb have been demonstrated for some of these compounds (Sailor, 1997).

Metal ion catalysts have been used to hydrolyze phosphate esters, including the organophosphate nerve warfare agents. GB (sarin) contains a phosphorus-fluorine bond that is hydrolyzed more rapidly in the presence of such catalysts (see Figure 5-17). When a copper metal ion catalyst is incorporated into the surface oxide of a porous silicon Fabry-Pérot film, a sensor that is highly specific for organofluorophosphonates results. The metal ion catalyst promotes a reaction between the organofluorophosphonate and water to produce hydrofluoric acid that dissolves the thin silicon dioxide film. The reaction results in a shift in the Fabry-Pérot interference fringes that can be monitored with an inexpensive, low-powered diode laser and phototransistor combination (see Figure 5-18). The device is specific for the vapors of sarin and presumably any members of the class of organofluorophosphonates (including diisopropylfluorophosphonate, soman, and cyclosarin (GF)) (Sohn et al., 2000).

Such materials could be used as triggers; they could be used in cheap, low-power devices that could sound an alarm in case of a leak.

### Lab-on-a-Chip Technology

Investigators at Arizona State University, the Naval Research Laboratory, and University of California, Riverside, have developed an integrated chip-based sensing device. Field detection of such hazardous substances as chemical warfare agents requires that powerful analytical performance be coupled to miniaturized low-powered instrumentation. “Lab-on-a-chip” devices, in which liquids are manipulated in a microchannel network, offer great promise for converting large and sophisticated instruments into powerful, field-deployable analyzers. Particularly attractive for on-site security applications are microchip devices that offer an analyzer with a very small footprint, a high degree of integration, high performance, fast response, and versatility (Wang, 2004). Such microfluidic devices offer great promise for transporting the forensic laboratory to the sample source, providing an early warning prior to terrorist activity, providing rapid postanalysis “fingerprinting” of a disaster site, and monitoring the cleanup of contaminated/remediated sites. Owing to their small footprint, microchip devices could perform multiple assays simultaneously. Self-contained microchips based on capillary electrophoresis (CE) with electrochemical detection are extremely attractive for on-site security applications, owing to the inherent miniaturization,

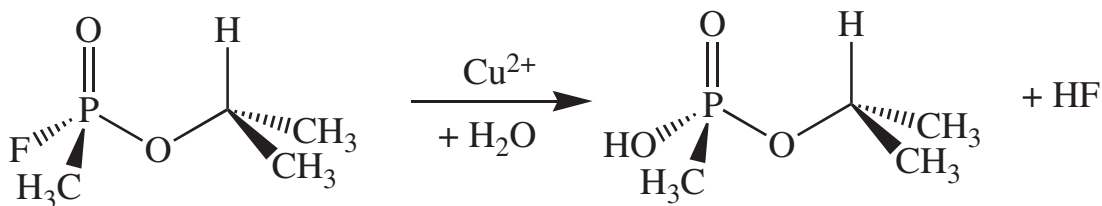


FIGURE 5-17 Metal ion catalysts containing a phosphorus-fluorine bond.



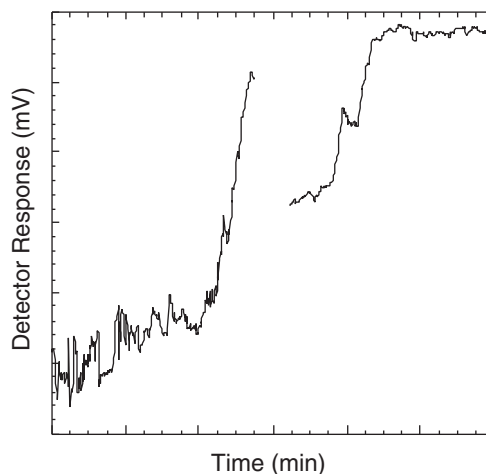


FIGURE 5-18 (Left) Handheld nanosensor device for nerve agent developed for the Micro Unattended Ground Sensors program (program manager: Edward Carapezza) of the Defense Advanced Research Projects Agency. The device contains a porous Si photonic crystal which contains chemistry that allows it to respond specifically to sarin (GB) gas. (Right) Testing run showing response to sarin at 10 ppm within 7 minutes of introduction. The sampling chamber was depleted of agent approximately 10 minutes into the run. SOURCE: Courtesy of M.J. Sailor, University of California, San Diego, and Kwok Ong, Aberdeen Proving Ground/Edgewood Arsenal.

high performance, low cost, and minimal power demands of such detectors.

Several microchip protocols for monitoring chemical agents and their degradation products have been developed (Wang et al., 2004a, 2004b, 2002a). They include the following:

- Precolumn enzymatic (organic phosphate hydrolase—OPH) reaction of organic phosphate nerve agents coupled to fast CE separation and amperometric detection of the nitrophenol reaction products (Wang et al., 2004a).
- A chip-based CE/conductivity microfluidic device that was recently developed for fast screening of chemical agent degradation products (Wang et al., 2002a). The miniaturized system relies on an efficient, chip-based separation of alkyl methylphosphonic acids (breakdown products of sarin, soman, and VX nerve agents) followed by sensitive conductivity detection. For example, Figure 5-19 displays an electropherogram for a river sample, spiked with 20 ppm methylphosphonic acid (a), ethyl methylphosphonic acid (b), and isopropyl methylphosphonic acid (c).
- CE microchip separation and amperometric detection of thiol-containing degradation products of V-type nerve agents (Wang et al., 2004b). The microchip assay relies on the derivatization reaction of 2-(dimethyl-

amino)ethanethiol, 2-(diethylamino)ethanethiol, and 2-mercaptoethanol with o-phthaldialdehyde (in the presence of the amino acid valine) along with amperometric monitoring of the isoindole derivatives. Typical assay times are 2 to 3 minutes.

Analogous microchip monitoring of explosive compounds has also been very successful (Wang et al., 2002b). Current efforts by these investigators are aimed at integrating sampling and preconcentration capabilities and at integrating multiple assays on a single microchip platform.

### Summary of Chemical Sensor Technology

The chemical sensor technologies described above represent new research directions. It is important to note that while some of the technologies are being pursued commercially, others are still at the academic laboratory stage. None of the technologies has been tested thoroughly with live chemical agents in diverse background environments. They also have not been tested for their longevity or false-positive/false-negative rates under realistic test conditions. While some of the methods have demonstrated an ability to detect ppb levels of agent, others have only ppm sensitivity. The advantage of most of the systems described here is that they are or could be designed to be small, low-power devices, and they have the potential to be inexpensive and fast. As such, these units

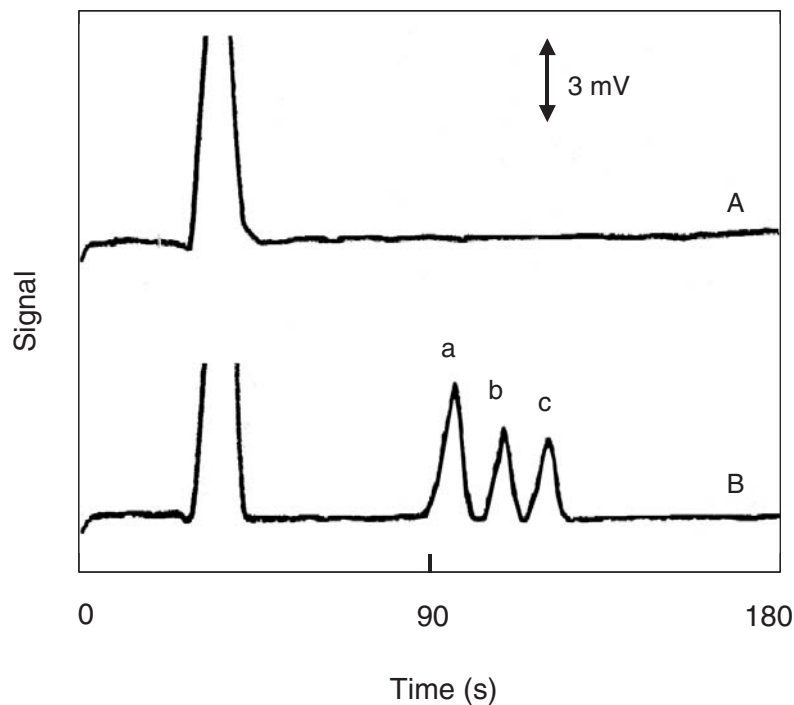


FIGURE 5-19 Peaks exiting the capillary electrophoresis (CE) chip: (a) methylphosphonic acid, (b) ethyl methylphosphonic acid, and (c) isopropyl methylphosphonic acid. SOURCE: Reprinted with permission from Wang et al., 2002a. Copyright 2002 by American Chemical Society.

could be used for detecting leaks at higher levels than those for worker protection (e.g., in storage igloo monitoring). If these sensors can be made small and inexpensive, they could be distributed throughout a facility and networked to provide early alerts for any localized releases of agent at threatening levels. If these advanced concepts are to be used in the time frame of the stockpile demilitarization effort, an accelerated development program will need to be put in place to take them from proofs of concept to commercialization.

**Finding 5-4.** During the time remaining for the CMA program, new chemical sensor technology is not likely to be useful for demilitarization plant monitoring at the STEL regulatory levels or below. The lead times for developing engineering prototypes and validating the technology with real chemical agents are long and are inconsistent with the program needs.

**Finding 5-5.** Chemical sensors have the potential to be useful for making rapid measurements at IDLH levels and above, such as for events including spills and leaks.

**Finding 5-6.** For any of the chemical sensors described, the federal government will be the customer, as there are no significant commercial markets for chemical agent detection. In order to take advantage of these technologies in the requisite time frame, accelerated support mechanisms must

be put into place to transition them from research to commercial utility. Chemical sensors developed for active military or homeland defense purposes might be adopted by the Chemical Materials Agency for real-time detection of high agent levels if these sensors become available before the demilitarization program ends.

### TECHNICAL MATURITY OF INNOVATIVE MONITORING TECHNOLOGIES

In this chapter, the committee identified real-time or near-real-time technologies that are based on measurement principles that differ from those currently being used for chemical agent monitoring at Army stockpile sites and that have the potential of being applied to agent vapor detection. Table 5-1 summarizes the advanced sensing technologies evaluated and notes sensitivity ranges and current limitations.

While long-path optical detection techniques such as DOAS or FT-IR could in principle possess multiagent capability, they do not appear to possess the requisite sensitivity for real-time monitoring at the new STELs. However, they may provide backup monitoring for large, uncontained releases of agent. In any case, these techniques are severely limited by interference from other atmospheric components, such as volatile organic compounds (from both natural and anthropogenic sources) and rain, fog, or haze. Surface-enhanced Raman spectroscopy may be a promising optical

TABLE 5-1 Summary of Potential Innovative Chemical Agent Monitoring Technologies

| Methodology  | Sensitivity  | Limitations  |
|--|--|--|
| UV differential optical absorption spectroscopy (DOAS)       | ppb under optimum conditions   | Lack of suitable UV absorbance; interference by atmospheric components, rain, haze, atmospheric turbulence.          |
| Open-path Fourier transform infrared (OP/FT-IR) spectroscopy | >0.001 mg agent/m <sup>3</sup> , i.e., >0.1 ppb under optimum conditions, for measurement times of several minutes | Interference by atmospheric components, rain, haze, atmospheric turbulence.  |
| Surface-enhanced Raman scattering (SERS)                     | tens of ppb  | Not real time; lack of reproducibility and regeneration of SERS substrates.  |
| Chemical ionization mass spectrometry (CIMS)                 | sub-ppt under optimal conditions   | Optimizing sensitivity and specificity; product development needed to go from custom instrument to commercial units. |
| Ion mobility spectrometry (IMS)                              | ppb to 10 ppt  | Unacceptably high level of false positives.  |
| Chemical sensors   | “low ppb” levels; mg/m <sup>3</sup> (Nomadics)   | Most are laboratory prototypes, not commercially available.  |

technique, but it is not real time, and it is unlikely to be any more sensitive than the ACAMS is. Also, it is probably less selective and more subject to interference from other airborne molecules.

Chemical ionization mass spectrometry is a very sensitive real-time technique for measuring concentrations of trace molecules in the atmosphere. The existing instrumentation is complex and expensive (compared with gas chromatographic instruments such as ACAMS or DAAMS). However, requirements for atmospheric monitoring have led to the development of robust, relatively compact, low-power-demand field instruments that could be adapted for chemical agent detection and monitoring at chemical agent demilitarization facilities.

A great deal of ongoing research on chemical sensors is directed toward the development of molecular-level devices that acquire, process, and sense the presence of specific analytes. These sensors are small and inexpensive—attributes that would make them suitable for wide deployment in chemical demilitarization facilities. However, while these sensors have the potential to be useful for making rapid measurements at IDLH levels and above, they are not sensitive enough for GPL or other regulatory-level measurements. In addition, most of these devices are still in the laboratory prototype stage and would require significant investment to make them commercially available.

The introduction of any innovative measurement technology will require intercomparison with accepted measurement protocols and systems (primarily ACAMS and DAAMS) to be able to meet regulatory requirements. Continuing validation and testing of any instrument are also required in order to ensure reliability. This presents an obvious difficulty with proposed open-path measurement techniques such as fence-

line FT-IR spectroscopy, since live testing with actual agents in an open atmosphere will not be acceptable to the Army or communities.

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## 6

# Opportunities for Improved Chemical Agent Monitoring

The preceding chapters reviewed chemical agent monitoring requirements and challenges, the present systems in use at operating chemical stockpile demilitarization facilities, and the types and capabilities of available monitoring alternatives. It is clear that the present monitoring systems are functioning adequately to protect the health and welfare of workers as well as of the neighboring public. The monitoring systems are distributed throughout the demilitarization facilities and are integrated with plant operating and maintenance procedures, control systems, and systems for the early detection of malfunctions or leakages. Given that the disposal operations will be on-going for some years, at least until 2012 and perhaps beyond, this chapter focuses on the possible use of new, potentially real-time measurement technologies that are compatible with the existing monitoring systems or which provide supplemental capabilities that address some other needs.

### PRESENT MONITORING NEEDS AND CAPABILITIES

The chemical agents stored and processed at stockpile sites were designed for use in warfare and therefore have the potential to cause fatal or chronic illnesses, depending on the type of agent, the concentration level, and the time of exposure. In combat, these agents are explosively deployed or sprayed to create aerosols that maximize airborne agent concentrations in target areas.

In stockpile storage, the munitions are stored in igloos and are inspected periodically for leakage. Any munitions that are found to be leaking are overpacked to provide secure containment. Agent stored in bulk (ton containers and spray tanks) has no explosives or propellants present and may be stored in open yards or warehouses. When munitions or bulk containers are transported to a processing facility for disposal, they are generally loaded by workers wearing protective gear into a secure, explosion-resistant container for movement to the unpack area of the facility. Mobile, near-real-time (NRT) airborne agent monitors are used for the

periodic checks of igloos for leaking munitions and in areas where munitions or bulk containers are being loaded and transported to processing buildings. After being unloaded from the transport container, the munitions and bulk containers are moved into the processing facility.

The processing facility is designed so that contaminated air within the facility is kept at a pressure below the outside pressure, preventing the leakage of contamination from inside to outside under normal operations. In the receiving area at the plant, the carrier containers are opened and the munitions or bulk containers of agent are moved into the plant. In the unpack area, pallets of munitions are opened and individual munitions are fed into the plant for processing. Demilitarization is conducted in campaigns during which only one type of agent is processed at a time. Agent monitors in the plant are calibrated only for the agent being processed in the current campaign (or, during the changeover periods between agent campaigns, for the previously processed agent and the agent about to be processed). Agent release from a misidentified munition containing a different agent therefore might not be detected by the monitors, although it might be detected by inspection.

Inside the processing area, ventilation systems are designed to keep agent-contaminated air inside the plant, and charcoal filters treat the exhaust air to prevent agent discharge into the atmosphere. However, in the unpack area and the munitions-handling area, agent-contaminated air is not usually present, and workers do not wear masks unless there is a STEL alarm. The STEL alarm is not instantaneous because of the nature of the current monitors—a measurement may take several minutes to register an alarm.

In processing facilities at incineration plants, agent is drained from munitions and containers and burned in a special furnace. This furnace is brought up to temperature using a conventional fuel before the agent feed is started. The combustion gases from the primary furnace chamber pass through a secondary “afterburner” chamber where additional mixing with atmospheric oxygen and lengthened

exposure to high temperature ensure essentially complete combustion of the agent. From the afterburner, gases are further treated and cooled before being exhausted through the stack. In the three third-generation incinerator plants built after the TOCDF, treated and cooled exhaust gases are directed through an activated-carbon filter bed that removes any residual agent or other semivolatile pollutants prior to discharge through the stack. Air monitors in the stack continually test the exhaust gases for agent emissions at the *source emission limit* (SEL), which was formerly termed the *allowable stack concentration* (ASC). Although the terminology has changed, the values for emission limits have not. Furthermore, carbon monoxide emission levels in the stack are monitored as a means to check that the furnace combustion processes are operating within design limits. If the stack alarm sounds or if the furnace temperature or carbon monoxide levels are out of normal range, the feed of agent to the furnace is automatically stopped.

Other furnaces in the facility that treat energetics, metals, and packing materials, along with some residual agent, also

have exhaust gas treatment systems and discharge through the activated-carbon filter bed to the common plant stack. These precautions make it essentially impossible for large amounts of agent to be discharged from the stack. Even if trace amounts should briefly be emitted from the stack, they further disperse, so general population limits (GPLs) for exposure to agents would not be exceeded at the property line.

Table 6-1 summarizes major airborne agent monitoring objectives during chemical weapons storage and demilitarization processing of the U.S. stockpile, and relates how the present monitoring systems (described in detail in Chapter 4) are used to assure that these objectives are met. A review of Table 6-1 confirms that most of the monitoring objectives are currently met satisfactorily. However, ACAMS, MINICAMS, and DAAMS all use the same type of gas chromatography-based separation and detection technology. There are multiple monitors that use the same measurement principles in the operational areas of the facilities to provide some redundancy, but there is no independent technology based on different measurement principles in place to pro-

TABLE 6-1 Present Goals and Capabilities of Monitoring Systems

| Objective   | Monitoring Systems and Capabilities   |
|---|---|
| Assurance that non-stockpile workers and the general public are not exposed to low-level agent exposures that might harm their health over the lifetime of operations.  | Historic (DAAMS) monitors capable of measuring concentrations at or above the GPL are deployed at locations around the property line to provide assurance that concentrations of airborne agents at or above the GPL are not present.   |
| Assurance that airborne agent exposures to each worker do not exceed CDC guidelines for worker protection during his or her employment at the facility, whether while working in safe areas or in areas requiring use of appropriate protective gear.   | Near-real-time (ACAMS or MINICAMS) monitors, calibrated to detect any airborne agent concentrations at or above the STEL, are deployed throughout the facility and are set to alarm at a level at which workers must don appropriate protective gear. Similar NRT monitors are also used to monitor higher agent concentrations in contaminated plant areas.  |
| Assurance that the disposal facility is operating reliably and safely, and that any operational upsets or agent leaks are quickly addressed in a protective manner.   | ACAMS or MINICAMS along with DAAMS at each location are also used to identify any malfunctions leading to airborne agent leakage in the facility. Sometimes an alarm is a false positive. Usually the cause is a lubricant, pesticide, or other substance that also activates the agent detector in the monitor. False positives are treated as real until they are proven false by analysis of the DAAMS sample, so too many false positives can impede plant operation. At baseline plants, ACAMS in the plant common stack are set at the SEL. They alarm and shut down agent feed to the furnaces if an exceedance is detected. |
| Assurance that extreme accident possibilities are controlled to the extent feasible, both in the plant and in the storage area, and that effective emergency response plans are coordinated with surrounding community response services.   | In addition to the many ACAMS or MINICAMS in the plant, portable units are used in the storage areas to inspect munitions in igloos or bulk storage areas. These instruments are also used whenever stockpile items are being moved to the processing area for demilitarization. Some of these portable monitoring units might also be useful in response to a major release.   |
| Assurance that, during closure operations, workers, the environment, and the public are protected as the plant is dismantled and contaminated materials are disposed of and, upon closure, the site is free from any agent residues that might jeopardize public or environmental well-being in the future. | Additional NRT monitors are deployed for all agents processed at the demil facility. Additional specialized monitoring techniques are used in closure; these are beyond the scope of this report.   |

NOTE: See Chapter 2 in this report for descriptions of monitoring levels.  
 SOURCE: Committee on Monitoring at Chemical Agent Disposal Facilities, 2004.

vide timely confirmation. Analytical instruments based on different measurement principles generally respond quite differently to potential interferent species. Since most false-positive detections by the current monitoring systems are due to interferents, employing a second detection method, unlikely to be “fooled” by these interferents, can significantly enhance overall system reliability.

Areas for potential improvements in airborne agent monitoring systems include the following:

- *Multiagent monitoring capabilities.* ACAMS are calibrated to detect one agent at a time. Although there is no evidence of an agent type within a munition having been misidentified in operations to date, there is a remote possibility that this might happen. Multiagent monitoring capability, even if at a much higher level than the STEL, might be of most use in the unpack area of the facility. It would also be useful during the closure operations of chemical demilitarization plants at multiagent stockpile sites when it is necessary to monitor simultaneously for all agents processed during plant operations (NRC, 2002b).
- *Shorter time intervals to setting off an alarm or to confirming or denying an alarm.* Shorter time intervals would be particularly desirable at the low-concentration monitoring levels required to meet recently revised CDC guidelines for agent airborne exposure limits. Rapid detection of agent releases within unpack areas might enhance worker safety, even at levels above the STEL.
- *Better capabilities for detecting an incipient major accident and tracking the resulting agent release plume.* Accidents so severe that they have potential for off-site impact are limited to scenarios in which large quantities of agent might be released in a short period of time. Site risk assessments identify the main causes and nature of such events, which are discussed later in this chapter as release scenarios. Depending on the scenario, air monitors might play a role in the early identification of such events and the notification of emergency services. By detecting or tracking the agent release plume, air monitors may also be useful in helping to identify effective emergency responses. In certain plant areas with the potential for serious accident events, air monitoring would be most useful around the higher levels, AEGL-1 or AEGL-2, which can be tolerated for an hour without irreversible health effects. If this monitoring used a real-time (nonchromatographic) technique, it would also provide both a prompt and an independent means of detecting, and, if deployed on a mobile platform, of tracking a major release.

The following sections present a discussion of release scenarios that might lead to a significant agent release beyond the boundaries of the Army depots containing chemi-

cal weapons stockpile storage areas and demilitarization facilities and describe the potential utility of systems to detect and track such releases.

On the basis of its analyses of the current airborne agent monitoring systems (see Chapter 4) and the monitoring requirements within and near the demilitarization facilities (summarized in Table 6-1), the committee concluded that the basic agent air monitoring system currently in place at stockpile storage and processing facilities seems capable of meeting the goals of protection for the public, workers, and the environment. Plant operability and worker safety might be further enhanced by improvements in sensitivity, selectivity, response time, and reliability of air monitors if such improvements are justified within the overall program goals. There may be a useful role for developing faster-warning higher-alarm-level monitors for certain critical work areas in order to provide more rapid warning to workers of a serious release of agent. Such monitors would not have to be as sensitive or selective as the existing monitors. If this higher-level-alarm monitor were to use a different technology from the existing gas chromatography-based instruments, it could provide an independent means for rapidly detecting or confirming a major release.

**Finding 6-1.** The current airborne agent monitoring systems are adequate to safely protect the chemical demilitarization workforce, the public, and the environment, although potential incremental improvements that enhance sensitivity and specificity to reduce the rate of false-positive alarms and/or shorten cycle times might improve plant efficiency and safety.

**Recommendation 6-1.** Continued incremental improvements in the current airborne chemical agent monitoring systems at chemical stockpile storage and demilitarization sites, as discussed in Chapter 4 of this report, should be pursued by the Army.

**Finding 6-2.** The unpack area is an area in chemical demilitarization facilities that process multiple munitions in which enhanced monitoring that features faster alarm response and/or multiagent capability might significantly enhance worker safety. An analysis of historic STEL alarms in such areas may indicate that worker protection could be enhanced by a more rapid alarm at a higher level, above the STEL but at or below the IDLH level or AEGL-1, that would allow faster masking of workers in the event of a large leak.

**Recommendation 6-2.** The Army should analyze whether the addition of real-time and/or multiagent monitoring in the unpack area of chemical demilitarization facilities that process multiple munitions would significantly reduce risk to workers who unpack and stage munitions for processing. If the risk analysis indicates a significant enhancement of worker safety, the Army should investigate whether other,

shorter response time and/or multiagent deployment modes for current NRT monitors or the development and/or procurement of real-time, multiagent monitors based on innovative technology are feasible and practical.

## PROSPECTS FOR IMPROVED AMBIENT RELEASE MONITORING

### Fence-Line Monitoring for Community Protection

The present systems for fence-line monitoring of chemical stockpile demilitarization facilities at the GPL appear adequate for providing a record that chronic agent emissions are not reaching the site property lines at levels that would involve a health threat to a member of the public, even for a lifetime of exposure. When false positives are eliminated, there has been only one documented indication that fence-line concentrations have ever exceeded the GPL level. In that case, a ton container of HD in the outdoor storage area at the Desert Chemical Depot in Utah leaked about 80 gallons of agent, and a signal at the GPL level was later detected by plant perimeter monitors about a mile from the spill (NRC, 2002a). The spill had been detected and cleaned up by the time the small signal from the perimeter monitor was analyzed and confirmed.<sup>1</sup>

In the absence of other indications of actual agent emissions penetrating beyond a site perimeter, the use of additional perimeter air monitors capable of measuring at such low levels may yield no significant benefit. Detection closer to potential release points is much more reliable and faster, given the capabilities of existing monitoring equipment.

### Demilitarization Facility and/or Storage Area Monitoring

Should a major agent release occur in a demilitarization plant or storage area, the fence-line monitors, as noted, are not a suitable means of warning, because they operate on long time scales and require laboratory analysis of collected samples to detect agent concentrations.

At present, the airborne agent monitors in the plant and portable monitors in the storage area that are designed to protect workers are also used as the main way of detecting any abnormal agent release. However, the alarm levels for these instruments are at the STEL, the appropriate limit for managing worker risks. Such STEL alarms from monitors in the working areas of the facility, or from the portable monitors where work is being performed in the storage area, do not represent an incident large enough to reach a site property line unless the alarms are associated with an accident that causes a release creating much higher concentrations.

In a storage area, portable monitors are only used when some operations are in progress. At other times, the storage area igloos are monitored for leaks only on a quarterly or annual basis, depending on the type of munitions being stored.<sup>2</sup> Even though the integrity of the stockpile is good, there is some possibility of releases that might not be detected promptly (NRC, 2004).

### Emergency Response to Major Events

In assessing the overall efficacy of current monitoring systems, it is necessary to look at accident possibilities that might cause extensive damage and perhaps impact the neighboring public. An examination of incidents that have occurred in the past at the operational chemical demilitarization facilities is one means to approach such an assessment. The NRC report *Evaluation of Chemical Events at Army Chemical Agent Disposal Facilities* examines a series of agent-related incidents that have occurred at stockpile facilities (NRC, 2002a). While that report examines a variety of incidents presenting potential risk to workers and makes a number of recommendations to improve worker safety, there were no reported incidents in which enough airborne agent crossed a facility boundary line to cause public risk.

Another way to identify possible accident scenarios is to hypothesize what might go wrong, how likely it is to happen, and what the resulting consequences might be under various weather conditions. To understand what sorts of accidents might have off-site impacts, it is useful to review the site-specific quantitative risk assessments (QRAs) prepared for the Army (U.S. Army, 2002a, 2003b, 2003c). These assessments include possible causes and estimates of the likelihood of potential major accidents, as well as estimates of the extent of the consequences for each scenario. Consequence models consider how much agent is released, release conditions, and the subsequent gradual dispersal of the plume through dilution by atmospheric mixing as the plume is carried downwind. Wind direction, speed, and atmospheric stability levels also determine rates of dispersal and the hazard zone for the plume.

The QRAs for the combined storage and disposal facilities at Anniston, Alabama; Tooele, Utah; and Umatilla, Oregon (ANCDF, TOCDF, and UMCDF) are the basis for the risk estimates shown in Table 6-2 for storage and processing during the estimated weapons-processing period (U.S. Army, 2002a, 2003b, 2003c). The numbers shown are a measure of overall public risk. It is evident that the risks of storage, even during the processing period, significantly exceed the risks

<sup>1</sup>Personal communication from Cheryl Maggio, Senior Project Engineer, CMA, to the committee at its November 22, 2004, meeting.

<sup>2</sup>Igloos containing nonoverpacked mines, projectiles, or bombs are required to be inspected for leaks on an annual basis according to the Army's storage monitoring and inspection (SMI) program. All other igloos, such as those containing M55 rockets and overpacked munitions, are inspected quarterly (NRC, 2004).

TABLE 6-2 QRA Public Risk Estimates for Three Sites

| Site                      | Duration of Processing Period | Chance of Having One or More Public Fatalities Over Processing Period Duration |                |
|---------------------------|-------------------------------|--|----------------|
|                           |                               | Storage  | Processing     |
| Anniston, Alabama (ANCDF) | 7 years                       | 1 in 750   | 1 in 1,800     |
| Umatilla, Oregon (UMCDF)  | 6 years                       | 1 in 2,100   | 1 in 3,300     |
| Tooele, Utah (TOCDF)      | 4 years                       | 1 in 10,000  | 1 in 1,100,000 |

NOTE: The risk estimates for TOCDF have been updated to reflect that all GB weapons have already been processed there; consequently, the overall level of remaining risk is much less than the level of risks at ANCDF and UMCDF. Risk estimates are for accidental agent releases and do not include releases due to sabotage or terrorist activities. (See discussion in text.)  
 SOURCE: U.S. Army, 2002a, 2003b, 2003c.

of processing. This is reasonable because of the smaller quantities in the processing area at any time, and because of the major layers of protection built in to the processing plant to contain any internal releases.

The Army has recently asked Science Applications International Corporation (SAIC) to use its QRA capabilities to establish “design basis” accident scenarios for the stockpile facilities (U.S. Army, 2003a). Since each site is different because of its location, weather, and surrounding populations, the scenarios were adapted to site-specific conditions. Table 6-3 shows recommended design basis accident source terms (that is, how much agent must be vaporized in the facility or storage area to cause a significant health risk to the nearest population). The likelihood of each design basis accident is in the range of 1 in 1,000 to 1 in 10,000 years; these are unlikely to occur during the lifetime of the plant but are not beyond credibility. The SAIC report (U.S. Army,

TABLE 6-3 Airborne Source Terms for Stockpile Sites from Design Basis Accident Scenarios

| Site                 | Evaluation Distance (km) | GB Vapor (kg) | VX Vapor (kg) | HD Vapor (kg) |
|----------------------|--------------------------|---------------|---------------|---------------|
| Tooele, Utah         | 3.4                      | —             | 2             | 100           |
| Anniston, Alabama    | 3.8                      | 20            | 1             | 50            |
| Umatilla, Oregon     | 2.9                      | 30            | 2             | 90            |
| Pine Bluff, Arkansas | 0.9                      | 5             | 0.3           | 20            |
| Blue Grass, Kentucky | 1.8                      | 10            | 1             | 40            |
| Aberdeen, Maryland   | 2.0                      | —             | —             | 40            |
| Pueblo, Colorado     | 2.5                      | —             | —             | 90            |
| Newport, Indiana     | 1.1                      | —             | 1             | —             |

SOURCE: U.S. Army, 2003a.

TABLE 6-4 Airborne Exposure Limits (AELs) (2005 values) and Vapor Pressure of Agents

|                            | Concentration Level of Agent (mg/m <sup>3</sup> ) |                        |                      |
|----------------------------|---|------------------------|----------------------|
|                            | GB  | VX                     | HD                   |
| GPL                        | 1 × 10 <sup>-6</sup>                              | 6 × 10 <sup>-7</sup>   | 2 × 10 <sup>-5</sup> |
| STEL                       | 1 × 10 <sup>-4</sup>                              | 1 × 10 <sup>-5</sup>   | 3 × 10 <sup>-3</sup> |
| Stack SEL                  | 3 × 10 <sup>-4</sup>                              | 3 × 10 <sup>-4</sup>   | 3 × 10 <sup>-2</sup> |
| 1-hr AEGL-2                | 3.5 × 10 <sup>-2</sup>                            | 2.9 × 10 <sup>-3</sup> | 1 × 10 <sup>-1</sup> |
| IDLH limit                 | 1 × 10 <sup>-1</sup>                              | 3 × 10 <sup>-3</sup>   | 7 × 10 <sup>-1</sup> |
| Saturated vapor 25°C       | 2.2 × 10 <sup>4</sup>                             | 1 × 10 <sup>1</sup>    | 7 × 10 <sup>2</sup>  |
| Saturated vapor/IDLH limit | 220,000   | 3,000                  | 1,000                |

SOURCE: Based on data provided to the NRC Committee to Assess Designs for the Pueblo and Blue Grass Chemical Agent Destruction Pilot Plants, and data from Abercrombie, 2003.

2003a) also develops design basis release source terms for workers within a 600 meter radius; the worker source terms generally are around 1 to 10 times higher than those for the public. Note that the design basis release probabilities were developed only for accidental agent releases; the probabilities of deliberate releases triggered by sabotage or terrorist attack are not included.

### POTENTIAL MAJOR RELEASE SCENARIOS

In this section, the information presented earlier is used to consider several spill scenarios, to examine how current monitoring would respond, and to identify what additional monitoring might be useful. Table 6-4 summarizes information (discussed in detail in Chapter 2) on agent exposure limits and vapor pressure parameters for GB, VX, and HD. This information is important in assessing the consequences of different sorts of releases.

In risk assessment studies, the focus is on accidents that have the potential to cause fatalities among the public. In assessments of risk, the Army sometimes uses a dose criterion (concentration multiplied by exposure time) that would cause 1 percent lethality in exposed populations.<sup>3</sup> Table 6-5 presents the 1 percent lethality dose for the agents of interest and also shows the exposure time at the IDLH limit that would give the 1 percent lethality dose.

#### Scenario 1: Liquid Agent Spills

Simple spills of agent generate vapor by evaporation from the liquid pool. The vapor pressure is important because it

<sup>3</sup>The Army more recently is using the AEGL-1 and AEGL-2 values in its emergency response planning activities.



TABLE 6-5 One Percent Lethality Doses for Agents and Exposure Times at IDLH Limit

| Agent Type | 1% Lethality Dose (mg-min/m <sup>3</sup> ) | Time (min) at IDLH to Give 1% Lethality Dose |
|------------|--|--|
| GB         | 10   | 100  |
| VX         | 4.3  | 1,400  |
| HD         | 150 <sup>a</sup>                           | 200 <sup>a</sup>                             |

<sup>a</sup>Level corresponding to maximum exposure with no permanent skin injury, rather than 1 percent lethality.

SOURCE: NRC, 1984.

represents the maximum concentration of agent vapor in the air above a surface of liquid agent. Both HD and VX have relatively low vapor pressures at ambient temperature. GB has higher volatility, similar to that of water, but is less toxic than VX. The last row of Table 6-4 shows the ratio of the vapor pressure to the IDLH AEL for the relevant chemical agent.

Thus, the higher vapor pressure of GB has consequences in terms of the extent of the hazard zone that can result from a spill. For example, if the contents of ton containers of HD or VX spill, the Army has estimated radial hazard zones for workers of about 80 feet or less (NRC, 1984). For a similar release of GB, one would expect a higher hazard zone because of its higher volatility—perhaps by a factor of about 10, since its ratio of vapor pressure to IDLH limit is about 100 times greater.<sup>4</sup> An estimate for GB is also described in an early NRC report (NRC, 1984, p. 37):

As an example of a calculation, the panel asked the personnel at Umatilla to calculate the 1% lethality distance for a large spill of GB resulting from the rupture of a 750 pound bomb. The assumptions of the calculations were as follows: 70°F temperature, 3 m/s wind speed, stability class F, 25% of the agent in the bomb spilled, and 30 minutes elapsed until the spill was covered. (Umatilla personnel noted that a plastic sheet is kept in readiness when such munitions are handled and that 10 minutes is more realistic as the time needed to cover the spill.) The resulting 1% lethality distance was computed to be 200 meters (about 600 feet).

The Army procedure is to rapidly cover any liquid agent spill with emergency tarps to further reduce vaporization. The spills are then treated with decontamination solutions to destroy the agent. Mobile air monitoring units are available to identify concentrations in the work areas around the spill so that workers are protected from exposures adverse to health.

<sup>4</sup>As vapor disperses, air mixes in from the side and top of the plume, so concentrations drop more than linearly with downwind distance.

In the QRAs for ANCDF, TOCDF, and UMCDF, simple spills of liquid appear significant only with respect to worker risk, since the vaporization rates from spills produce concentrations of airborne agents that will be highly diluted before they can reach a location where the public could be exposed.

### Scenario 2: Explosive Dispersion of Agent

The more hazardous events associated with the stockpile are those that involve explosive dispersion of agent. In early studies of stockpile risks, a “maximum credible event” was taken to be an explosion of an igloo full of M55 GB rockets. The igloos are spaced so that explosions in one igloo are very unlikely to set off an explosion in an adjacent igloo. Igloos with M55 rockets currently exist at four of the stockpile sites. The Army calculated 1 percent lethality distances for an explosion of an igloo containing GB M55 rockets. It was assumed that about 97 percent of the agent was consumed in the explosion and subsequent fire, based on some evidence from tests conducted at the Black Hills Army Depot in South Dakota and the Dugway Proving Ground in Utah. Those tests also showed that for M55 rockets, sympathetic detonations could spread throughout rockets stored in the same igloo. The Army also found that the explosion of one land mine in a three-mine container might detonate the other two mines, but that sympathetic detonation in other containers of munitions does not occur.<sup>5</sup>

Using the explosion of an igloo of GB M55 rockets as an extreme accident scenario, the Army computed downwind dispersion distances for 1 percent lethality and found that hazard zones extended about 5 miles from the source under typical daytime conditions and up to about 27 miles at night, when the height of the mixing layer is much lower (Irving et al., 1970; Lloyd, 1994). Other major scenarios included detonation of a 155 mm GB round, creating 1 percent lethality at a distance of 3,000 feet, and detonation of a 155 mm HD round, creating irreversible skin damage up to 260 feet.

Therefore, the risks to the public from the stockpile are associated with major explosions that might be caused by accidental detonation of an M55 rocket or rockets during handling or by detonation as a result of some natural disaster (e.g., lightning strike, earthquake), a plane crash, or sabotage. For the Tooele facility, for example, the site risk assessment shows that over 82 percent of all the average public fatality risk from the storage facility is initiated by seismic events, with 11 percent from a GB container leak<sup>6</sup> and 4 percent

<sup>5</sup>Reference material sent by Marilyn Daughdrill (then Tischbin), Chemical Materials Agency, to Don Siebenaler, NRC Senior Program Officer, May 9, 1997, described as information to accompany an Army videotape, Project ID 7VA-1334-0004-SP86.

<sup>6</sup>All GB ton containers have now been demilitarized at TOCDF. There are no more GB ton containers in the stockpile.



from lightning (NRC, 1997). At Umatilla, 97 percent of the storage risk to the public is from seismic events (U.S. Army, 2002b). For Anniston, public risks from storage are dominated by lightning strikes (84 percent), seismic events (9 percent), and errant rounds from the Pelham firing range (6 percent) (U.S. Army, 2002c).

While air monitors are used to check for leakages in the stockpile, it is unlikely that air monitors would be of relevance to improved detection of such an extreme igloo detonation scenario. Portable or mobile units might be of use in detecting and tracking downwind concentrations of agent in the aftermath of a major release. If the Army has not already done so, it should evaluate how useful its current monitoring equipment might be in such an accident response mode and in conjunction with the response plans of local emergency services. While fixed-site NRT monitors might provide useful indications of agent-contaminated areas, the actual tracking of a dispersing plume requires real-time monitors deployed on mobile ground or air vehicles.

### Scenario 3: Major Releases in a Processing Facility

In the original QRA for TOCDF, over 97 percent of the public risk from processing was due to seismic events that caused collapse of major portions of the processing facility (U.S. Army, 1996). In the more recent QRAs for TOCDF (updated after the completion of GB campaigns), ANCDF, and UMCDF, the leading cause of public risk (around 90 percent) comes from a number of fire-initiated major accidents that spread within the facility. Some of these events included fire damage to ventilation systems and the carbon filter beds. In both fire and natural disaster scenarios, the usefulness of air monitoring equipment is likely to be compromised. At other sites where a QRA is not currently available, the causes of risk may shift to other sorts of serious initiating events. Nonetheless, rapid reporting of fires within a plant needs to be a major part of any emergency response program on site and should include off-site emergency services. Here again, the availability of portable real-time or near-real-time or mobile real-time monitoring equipment might be useful in the aftermath of a release. Also, since fire is a major contributor to risk in both disposal and storage facilities, fire detection, alarm, and suppression equipment are additional elements of protection, and fire prevention activities may also help prevent significant agent release events.

### Summary of Major-Release Scenario Analyses

To pose an acute risk to the public, the atmospheric release of sufficient chemical agent vapor or aerosol would require a major accident. A careful review of portable air monitoring equipment now used to protect storage area workers should be conducted to evaluate the role that such equipment might play in responding to major disasters with the potential for off-site impact. The development of innova-

tive, dispersed portable or mobile real-time agent monitors operating between the STEL and IDLH levels would allow rapid detection and, potentially, the tracking of a significant release plume. The development of such capabilities might be coordinated with the Department of Homeland Security, which may have similar chemical agent monitoring requirements.

**Finding 6-3.** To pose an acute risk to the public, the atmospheric release of sufficient chemical agent vapor or aerosol would require a major accident, almost certainly involving explosion and/or fire. The ability to confirm dispersion model predictions that an agent plume has penetrated the depot boundary and threatens the public or to track the agent plume would require fast-response monitors operating at levels between the STEL and the IDLH that are either widely dispersed or are mounted on a suitable ground or air mobile platform.

**Recommendation 6-3.** The Army and other relevant stakeholders should assess whether public protection would be significantly enhanced by the development and deployment of dispersed fixed or portable fast-response agent sensors or the development of a mobile fast-response agent sensor platform capable of detecting and tracking a large release plume.

### Applicability of Identified Advanced Monitoring Technologies for Agent Release Scenarios

As stated in Chapter 5 and noted in the release scenarios analyses presented in this chapter, the primary reasons to consider using advanced agent monitoring technologies are to shorten measurement response times significantly without unduly sacrificing either sensitivity or specificity, and to deploy these instruments where rapid detection or confirmation of agent would provide significant protection to workers or the public. Two potential venues for enhanced agent monitoring have been identified by the committee: (1) faster response and, possibly, multiagent monitoring in the unpack areas of the demilitarization facilities; and (2) detection and tracking of a major-agent-release plume at agent concentration levels somewhere above the STEL but below the IDHL.

Of the advanced agent monitoring technologies evaluated in Chapter 5, only two appear to offer multiagent capability, real-time detection, and sufficient sensitivity and specificity for relevant chemical agents coupled with a significant demonstrated utility within the air quality/atmospheric chemistry community to warrant consideration for possible deployment at chemical disposal and storage sites. These are open-path or folded-path Fourier transform infrared spectroscopy and chemical ionization mass spectrometry.

As demonstrated in Chapter 5, in order to have fast enough response times and sufficient sensitivity for the relevant chemical agents, Fourier transform infrared systems must be deployed with either long open-path mirror systems

or a fairly large multipass gas cell into which high-volume air samples are drawn from multiple sampling lines. Note, however, that if contaminated air is only drawn from one of these sampling lines, as may be expected to be the case in the early stages of a release, the air in the cell is diluted by air drawn from the other lines, significantly increasing the limit of detection. In general, these systems will be too large for mobile deployment, and a single system can cover only a limited area, even with multiple open-path target mirrors or sampling lines into a multipass gas cell. Its utility for large-plume-release detection and quantification seems limited, since FT-IR systems would need to be deployed relatively near potential release points to avoid using a large number of units, although one organization has promoted this application.<sup>7</sup>

An open- or folded-path FT-IR system might be of utility as a fast-response detector in a demilitarization facility unpack area, an application briefly explored with some promise by the Army nearly a decade ago (Stedman and McLaren, 1996). As noted above, an unpack area FT-IR monitoring system could be deployed either in an open-path configuration, above the level where people or equipment would routinely block the infrared beam, or in a closed, multipath cell configuration with multiple sampling lines. Since the molecular weight of agent molecules is much greater than that of oxygen or nitrogen, they would tend to have higher concentration at ground level. Thus, their concentration at ground level may be dangerously underestimated by an elevated beam.

As demonstrated in Chapter 5, chemical ionization mass spectrometry (CIMS) is a far more sensitive analytical technique than is FT-IR spectroscopy for most semivolatile pollutants. CIMS is a point sampling analytical technique, although its very high sensitivity and rapid measurement capability can allow it to be coupled to multiple sampling lines or mounted on a mobile platform to provide significant spatial coverage quickly and accurately. An unpack area deployment would presumably monitor a number of sampling lines sequentially. A release plume detection and tracking deployment would most likely involve a mobile platform.

**Finding 6-4.** Open- or folded-path FT-IR and CIMS technology have some promise for providing enhanced, fast-response chemical agent monitoring capability to chemical weapons storage and demilitarization facilities. The most likely effective use for FT-IR spectroscopy is to provide fast-response, multiagent monitoring for a relatively restricted space such as a demilitarization facility's unpack area. CIMS instruments are likely to be far more sensitive chemical agent

detectors than are FT-IR instruments. Potential CIMS applications include monitoring a restricted space, such as a demilitarization facility's unpack area, through multiple sampling lines, and detecting and tracking a large-release plume mounted onboard a mobile van or small aircraft.

## TECHNICAL AND COMMERCIAL MATURITY OF PROSPECTIVE MONITORING TECHNOLOGIES

Potential supplemental chemical agent monitoring roles at chemical demilitarization facilities have been identified for two specific innovative real-time monitoring technologies: open-path Fourier transform infrared spectroscopy and chemical ionization mass spectrometry. In order to significantly impact the chemical demilitarization process, commercial versions of these instruments capable of sustained and effective operation in an industrial environment need to be available within 2 to 3 years. The commercial status of these two airborne chemical agent monitoring technologies is briefly reviewed below.

### Open-Path Fourier Transform Infrared Spectroscopy

OP/FT-IR spectroscopy is a relatively mature measurement technology that has been recognized by the U.S. Environmental Protection Agency as a reference method for airborne pollutant quantification. As early as 1997, an open-path FT-IR product review identified and evaluated commercial systems from five vendors (Newman, 1997). FT-IR systems are now widely used in both industrial process and emissions monitoring and in environmental field measurements. Ongoing improvements in optical, electronic, and computer technologies are prompting the continuous development of compact, rugged, and capable FT-IR systems, many of which can be deployed in open-path configurations. Several commercial FT-IR vendors and custom-instrument companies are capable of producing a version customized for chemical agent detection within a year; although it is unlikely that these instruments would have practical detection limits much below 1 ppb for any of the relevant chemical agents (see Box 5-1 in Chapter 5).

### Chemical Ionization Mass Spectrometry

As detailed in Chapter 5, CIMS instruments must be tailored for specific target molecules by demonstrating that the precursor ion species effectively ionizes the target agent, producing a unique product ion that is not compromised by large signals at the same  $m/z$  values produced from common potential interferents. While CIMS work in Army laboratories showed that various proton transfer reactive ions were efficient chemical agent ionizers, the more recently developed negative ion precursor systems, which produce extremely high sensitivities for many atmospheric pollutants, have not been tested with chemical agents. As noted in

<sup>7</sup>Optical Remote Sensing to Detect and Map Low Levels of Chemical Threat, presentation by Ram A. Hashmonay, Arcadis, to the Technologies for Chemical Agent Detection Workshop, Washington, D.C., August 24, 2004.

Chapter 5, computational and experimental studies to determine the extent which various negative precursor ions could improve real-time chemical agent detection levels could be quickly performed.

There is one commercial CIMS system currently available which uses  $H_3O^+$  as the precursor ion. It is produced and marketed by Ionicon Analytik in Austria. This instrument is widely used in airborne field measurements to map airborne organic pollutants without significant modification, and a moderately ruggedized version has been successfully deployed in a van-mounted vehicle laboratory to map ground-level organic pollutants and identify organic emissions plumes (Kolb et al., 2004). Based on the experience of committee members in developing and commercializing mass spectrometric instruments of similar complexity, the committee estimates that a commercial CIMS instrument optimized for GB, VX, and HD detection could be customized and produced for sale in moderate quantities within 2 years.

### ABILITY TO MEET REGULATORY REQUIREMENTS

There are no U.S. federal or state environmental regulations that set emissions standards for chemical agents or specify air monitoring requirements. For instance, since chemical agents are not designated by the EPA as either criteria pollutants or controlled air toxic species, maximum achievable control technology (MACT) rules do not apply to their emission control or emission monitoring technologies. Rather, these agent emissions are regulated under the RCRA permits that are issued for each site by the appropriate state environmental authority. As the Army adapts to the new AELs recommended by the CDC, it has modified its operational monitoring procedures throughout the chemical demilitarization program. The Army is now monitoring to the STEL (which is numerically equivalent to the former WPL/TWA) as the alarm point at which workers mask and operations stop until the source of the alarm is identified. Further, measurements are made at fractions of the STEL that are closer to the new WPLs for informational purposes. The new WPLs are monitored using the DAAMS equipment, which does not provide near-real-time information. Health records are maintained for all worker exposures that are significant so that longer-term health impacts from multiple exposures are controlled.

The implementation of the new AELs basically maintains the levels of protection that had been provided to workers prior to the revisions to the AELs promulgated by the CDC. However, the new nomenclature is not consistent with that found in existing RCRA permits at the sites. Therefore, the Army is seeking the necessary permit modifications at each of the sites and is updating its own procedures and documents accordingly. The meetings with the regulators are ongoing as of this writing and are progressing satisfactorily. In situations in which the new AELs are enacted before the permit issues have been satisfactorily resolved, the Army

will request temporary authorization to operate in the interim. Permits for sites not yet ready for operation will be based on the new requirements.

### SUMMARY OF OPPORTUNITIES FOR IMPROVED AIRBORNE AGENT MONITORING

The issue of whether or not to enhance the current airborne chemical agent monitoring systems at chemical weapons storage and demilitarization facilities is complex. The current monitoring systems are generally adequate and well integrated into facility operations. The addition of new technology would impose new costs, both for hardware and for additional staff, as well as added complexity to systems that are already difficult to manage and maintain effectively. Thus, the addition of any advanced monitoring capabilities need to provide benefits that are greater than the monetary and operational challenges they will impose.

In addition, new technology must be developed, demonstrated, acquired, and integrated into operations in a relatively short time if its benefits are to be exploited. Chemical demilitarization facilities have already destroyed over a third of the original stockpile and are not likely to operate more than 7 to 12 years longer. In the committee's opinion, this means that new monitoring technology needs to be developed and convincingly demonstrated within 2 to 3 years and acquired and integrated within 4 years if it is to have a substantial impact.

**Recommendation 6-4.** The Army should only deploy advanced chemical agent monitoring equipment after a thorough risk/benefit analysis shows that the risk reduction to the workforce and/or public justifies the monetary and opportunity costs.

**Recommendation 6-5.** If worker or public risk reduction analyses indicate significant benefit at acceptable cost from deployment of fast-response, multiagent monitoring capabilities, systems using FT-IR or, more likely, CIMS should be considered.

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## 7

# Findings and Recommendations

The findings and recommendations developed and presented in the previous chapters of this report are gathered below for easy review.

### GENERAL AIRBORNE CHEMICAL AGENT MONITORING CHALLENGES

**Finding 2-1.** The Army's use of CDC's newly promulgated short-term exposure limits (STELs) as a basis for monitoring at demilitarization facilities is appropriate to ensure that workers are protected.

**Recommendation 2-1.** The committee recommends that the Army continue to use short-term exposure limits (STELs) as the basis for near-real-time monitoring.

### AIRBORNE CHEMICAL AGENT MONITORING WITH CURRENT TECHNOLOGY

**Finding 4-1.** The Army has taken significant steps to reduce the level of false alarms (false positives) for ACAMS and MINICAMS monitors at stockpile disposal sites, especially through the elimination of potential chemical interferences and by the adjustment of alarm levels (while still maintaining a statistical response rate of 95 percent or better for the detection of agent excursions above 1.00 STEL). False-positive alarms are still a problem, however, especially when monitoring at VX STEL levels using NRT monitors. Also, false positives are expected to be a significant problem when using DAAMS monitors equipped with FPDs to monitor at the 2003/2004 WPLs and GPLs.

**Finding 4-2.** In accordance with the determinations of previous NRC studies (NRC, 1999, 2001<sup>1</sup>), the committee finds that the reliability of ACAMS, MINICAMS, and DAAMS

appears to provide sufficient airborne agent monitoring capability to afford adequate protection to workers, the general public, and the environment.

**Finding 4-3.** Air monitoring instrumentation used at stockpile disposal sites has been capable of reliable detection of the 1988 TWA levels for agents, as earlier NRC committees have indicated. These NRT instruments (ACAMS and MINICAMS) are likewise capable of detection at the 2003/2004 STEL and 2003/2004 IDLH levels.

**Finding 4-4.** DAAMS has proven effective in monitoring at the CDC's 1988 TWA and GPL levels at stockpile disposal sites for more than 15 years. Because the 2003/2004 STELs have the same numerical concentration values as the 1988 TWA levels, historical and confirmation monitoring of GB, VX, and HD at the new STELs using DAAMS will be no more difficult than monitoring these agents at the 1988 TWA levels. Also, monitoring at the 2003 WPL for GB using DAAMS will be straightforward, with no significant increase in the occurrence of false positives (compared with DAAMS monitoring for GB at the 1988 TWA level). However, although DAAMS either has or is likely to have adequate sensitivity for monitoring at 2003/2004 AELs, the frequency of false positives is expected to increase in the following cases:

- The 2003 VX WPL, which is less than the 1988 GPL for this agent;
- The 2004 HD WPL, which is less than the 1988 GPL;
- The 2003 GB GPL level, which is one-third of the 1988 GPL level;
- The 2003 GPL for VX, which is one-fifth of the 1988 GPL value; and
- The 2004 GPL for HD, which is one-fifth of the 1988 HD GPL value.<sup>2</sup>

<sup>1</sup>For references, see p. 37.

<sup>2</sup>As a consequence of the quadratic response of the FPD, the detector signal for the 2004 HD GPL will be 25 times less than the detector signal



**Finding 4-5.** The efforts of the Chemical Materials Agency (CMA) have resulted in the demonstration of significant incremental improvements in MINICAMS and DAAMS. It is clear, however, that even with the improvements demonstrated by the CMA, it will probably be difficult to monitor agents, especially VX and HD at the 2003/2004 GPL levels, without a significant increase in false positives (compared with monitoring at the 1988 GPL levels). Also, despite the success demonstrated to date, false positives may be a significant problem when monitoring at the 2003/2004 WPLs. Finally, false positives for ACAMS and MINICAMS monitors, especially when monitoring at the STEL for VX, are expected to continue.

**Recommendation 4-5.** The Chemical Materials Agency (CMA) should consider a wider range of incremental improvements to ACAMS, MINICAMS, and DAAMS to allow these monitoring systems to better monitor at the CDC's 2003/2004 AELs. Some technologies that deserve consideration by the CMA include the following:

- Adding a convex lens to the FPD to improve the signal-to-noise ratio of this detector in ACAMS, MINICAMS, and DAAMS;
- The use of cryotrap for all DAAMS monitors to sharpen GC peaks and thereby improve selectivity and sensitivity;
- The equipping of DAAMS systems with a PFPD in place of the FPD to enhance the selectivity and sensitivity of the DAAMS when monitoring for GB, VX, and HD;
- The equipping of DAAMS monitors with an XSD to enhance the selectivity and sensitivity of this system when monitoring for HD;
- The use of a sulfur chemiluminescence detector (SCD) for the detection of HD; and
- Funding the development of a phosphorus-specific FPD based on the magnetic quenching of  $\text{HPO}^{*3}$  emissions, a detector that is expected to be much more selective for organophosphorus compounds than is the conventional FDP or the PFPD.

**Finding 4-6.** The Army's plan to allow alarm levels for NRT monitors to be set at 1.00 AEL, especially for the CDC's 2003/2004 STEL and IDLH values, has the potential to be perceived by workers and the general public as a significant reduction in safety for workers; will result in widely varying alarm rates from instrument to instrument and from week to week; will increase the probability that a worker may be exposed to unacceptable levels of HD, a classified carcinogen; and will increase the likelihood that the Army will not

respond properly or in a timely manner to the presence of agents at true concentrations above the AELs. The only perceived benefit to raising the alarm level to 1.00 AEL is a possible reduction in the rates of false alarms, but this benefit is gained at the expense of a higher probability of false negatives.

**Recommendation 4-6.** The Army should consider continuing to use alarm levels that ensure that all properly operated and maintained NRT monitors at a given site have at least a 95 percent probability of sounding an alarm any time the true agent concentration in an area being monitored exceeds 1.00 STEL.

**Finding 4-7.** At some sites, state regulators may insist that alarm levels be set at 0.2 STEL, the lower limit of certification for NRT monitors, even though it is likely that a statistical response rate of 95 percent or better can be achieved with the alarm level set at 0.5 STEL. Although an alarm level of 0.2 STEL typically ensures at least a 99 percent probability of detecting a true agent excursion above 1.00 STEL, alarm levels this low contribute significantly to the frequency of false alarms observed at stockpile disposal sites and contribute to a reduction in worker safety caused by the human tendency to discount an alarm if false alarms are experienced frequently.

## AIRBORNE CHEMICAL AGENT MONITORING WITH ADVANCED TECHNOLOGY

**Finding 5-1.** In general, the use of FT-IR spectrometry with either open-path or multipass gas cell sampling for monitoring chemical warfare agents (CWAs) at levels below about  $0.05 \text{ mg m}^{-3}$  in the atmosphere near the perimeter of chemical agent storage facilities or demilitarization plants is not likely to be effective because of the low sensitivity of this technique. Conversely, FT-IR spectrometry may play an important role in monitoring accidental releases of chemical agents in locations very close to where the agents are stored or incinerated and where the concentration may exceed  $0.05 \text{ mg m}^{-3}$ . Detecting a catastrophic release within a minute of the event would allow suitable action to be taken.

**Finding 5-2.** Although SERS is the most promising infrared technique of any reviewed by the committee, it is unlikely to be any more sensitive or faster than ACAMS and probably would be less selective and more subject to interference from other airborne molecules.

**Finding 5-3.** Chemical ionization mass spectrometry (CIMS) is a highly sensitive technique that may be able to detect all chemical agents in real time, potentially even at the general population limit. Previous work has focused exclusively on positive ion precursors. Instruments in the atmospheric community extensively use negative ions as a precursor, leading to increased selectivity without sacrificing sensitivity. Commercial CIMS instrument are already available, although with reduced sensitivity.

obtained for the 1988 HD GPL (for the same sample flow rate and sample period). For this reason, it may prove very difficult to monitor for HD at the 2004 GPL.

<sup>3</sup>The asterisk symbol as used here indicates an excited electronic state.



**Recommendation 5-3.** The Army should investigate whether present CIMS instrumentation could be immediately used to detect chemical agents at the IDHL limit in real time. The use of negative ions as a precursor should be investigated to improve selectivity. Adaptation of one of the research-grade atmospheric field instruments for real-time detection between the STEL and the GPL for each relevant agent should be considered.

**Finding 5-4.** During the time remaining for the CMA program, new chemical sensor technology is not likely to be useful for demilitarization plant monitoring at the STEL regulatory levels or below. The lead times for developing engineering prototypes and validating the technology with real chemical agents are long and are inconsistent with the program needs.

**Finding 5-5.** Chemical sensors have the potential to be useful for making rapid measurements at IDLH levels and above, such as for events including spills and leaks.

**Finding 5-6.** For any of the chemical sensors described, the federal government will be the customer, as there are no significant commercial markets for chemical agent detection. In order to take advantage of these technologies in the requisite time frame, accelerated support mechanisms must be put into place to transition them from research to commercial utility. Chemical sensors developed for active military or homeland defense purposes might be adopted by the CMA for real-time detection of high agent levels if these sensors become available before the demilitarization program ends.

## SUMMARY OF AIRBORNE CHEMICAL AGENT MONITORING FINDINGS AND RECOMMENDATIONS

**Finding 6-1.** The current airborne agent monitoring systems are adequate to safely protect the chemical demilitarization workforce, the public, and the environment, although potential incremental improvements that enhance sensitivity and specificity to reduce the rate of false-positive alarms and/or cycle times might improve plant efficiency and safety.

**Recommendation 6-1.** Continued incremental improvements in the current airborne chemical agent monitoring systems at chemical stockpile storage and demilitarization sites, as discussed in Chapter 4 of this report, should be pursued by the Army.

**Finding 6-2.** The unpack area is an area in chemical demilitarization facilities that process multiple munitions in which enhanced monitoring that features faster alarm response and/or multiagent capability might significantly enhance worker safety. An analysis of historic STEL alarms in such areas may indicate that worker protection could be enhanced by a more rapid alarm at a higher level, above the STEL but at or below the IDLH level or AEGL-1, that would allow faster masking of workers in the event of a large leak.

**Recommendation 6-2.** The Army should analyze whether the addition of real-time and/or multiagent monitoring in the unpack area of chemical demilitarization facilities that process multiple munitions would significantly reduce risk to workers who unpack and stage munitions for processing. If the risk analysis indicates a significant enhancement of worker safety, the Army should investigate whether other, shorter response time and/or multiagent deployment modes for current NRT monitors or the development and/or procurement of real-time, multiagent monitors based on innovative technology are feasible and practical.

**Finding 6-3.** To pose an acute risk to the public, the atmospheric release of sufficient chemical agent vapor or aerosol would require a major accident, almost certainly involving explosion and/or fire. The ability to confirm dispersion model predictions that an agent plume has penetrated the depot boundary and threatens the public or to track the agent plume would require fast-response monitors operating at levels between the STEL and the IDLH that are either widely dispersed or are mounted on a suitable ground or air mobile platform.

**Recommendation 6-3.** The Army and other relevant stakeholders should assess whether public protection would be significantly enhanced by the development and deployment of dispersed fixed or portable fast-response agent sensors or the development of a mobile fast-response agent sensor platform capable of detecting and tracking a large release plume.

**Finding 6-4.** Open- or folded-path FT-IR and CIMS technology have some promise for providing enhanced, fast-response chemical agent monitoring capability to chemical weapons storage and demilitarization facilities. The most likely effective use for FT-IR spectroscopy is to provide fast-response, multiagent monitoring for a relatively restricted space such as a demilitarization facility's unpack area. CIMS instruments are likely to be far more sensitive chemical agent detectors than are FT-IR instruments. Potential CIMS applications include monitoring a restricted space, such as a demilitarization facility's unpack area, through multiple sampling lines, and detecting and tracking a large-release plume mounted onboard a mobile van or small aircraft.

**Recommendation 6-4.** The Army should only deploy advanced chemical agent monitoring equipment after a thorough risk/benefit analysis shows that the risk reduction to the workforce and/or public justifies the monetary and opportunity costs.

**Recommendation 6-5.** If worker or public risk reduction analyses indicate significant benefit at acceptable cost from deployment of fast-response, multiagent monitoring capabilities, systems using FT-IR or, more likely, CIMS should be considered.

# Appendixes



## Appendix A

### Biographical Sketches of Committee Members

**Charles E. Kolb**, *Chair*, graduated from the Massachusetts Institute of Technology with a B.S. in chemical physics and from Princeton University with an M.A. and a Ph.D. in physical chemistry. Dr. Kolb is president and chief executive officer of Aerodyne Research, Inc., in Billerica, Massachusetts. His principal research interests have included atmospheric and environmental chemistry, combustion chemistry, materials chemistry, and the chemical physics of rocket and aircraft exhaust plumes. He has served on several National Aeronautics and Space Administration and Environmental Protection Agency panels dealing with environmental issues, as well as on eight National Research Council (NRC) committees and boards dealing with atmospheric and environmental chemistry. Dr. Kolb also served on the NRC's Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program (member, 1993–1998; vice chair, 1998–2000) and on the Committee on Review and Evaluation of Chemical Events at Army Chemical Demilitarization Facilities (chair, 2001–2002). He has also been appointed a National Affiliate of the National Academies. He is a fellow of the American Physical Society, American Geophysical Union, American Association for the Advancement of Science, and Optical Society of America.

**Jeffrey I. Steinfeld**, *Vice Chair*, graduated from the Massachusetts Institute of Technology (MIT) with a B.S. in chemistry and from Harvard University with a Ph.D. in physical chemistry. He is currently professor of chemistry at MIT. He has taught and written extensively for more than 37 years at MIT, specializing in high-sensitivity monitoring techniques, pollution prevention, and environmental research and education. His experience is well suited to the work of a committee concerned with the safety and monitoring activities of the Army's Chemical Demilitarization Program. His interest and experience in bringing scientific knowledge into environmental decision making via stakeholder involvement are particularly applicable to the assessment of a disposal pro-

gram that has considerable political, economic, social, scientific, and technical impact.

**Elisabeth M. Drake**, a member of the National Academy of Engineering, graduated from the Massachusetts Institute of Technology (MIT) with a Ph.D. in chemical engineering. She retired in 2000 as the associate director of the MIT Energy Laboratory. Dr. Drake presently is an emerita staff member at the MIT Laboratory for Energy and the Environment. She has had considerable experience in risk management and communication; in technology associated with the transport, processing, storage, and disposal of hazardous materials; and in chemical engineering process design and control systems. She has served on several NRC committees relating to chemical demilitarization, and participated in an earlier NRC monitoring study within the Army Chemical Stockpile Disposal Program (1994) conducted by the Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program. Dr. Drake has a special interest in the interactions between technology and the environment. She belongs to a number of environmental organizations, including the Audubon Society and the National Wildlife Federation.

**Colin G. Drury** is UB Distinguished Professor and Chair of Industrial Engineering at the State University of New York at Buffalo, concentrating on the application of human factors techniques to manufacturing and maintenance processes. After receiving a Ph.D. from the University of Birmingham, UK, Dr. Drury became manager of ergonomics at Pilkington Glass. He has published extensively on topics in industrial process control, quality control, and aviation maintenance and safety, and he is North American editor of *Applied Ergonomics*. From 1988 to 1993, he was the founding executive director of the Center for Industrial Effectiveness. He is a fellow of the Institute of Industrial Engineers, the Ergonomics Society, the International Ergonomics Association, and the Human Factors Ergonomics Society. Dr. Drury re-

ceived the Bartlett Medal of the Ergonomics Society and the Fitts Award of the Human Factors Ergonomics Society, and has served on a number of NRC committees.

**J. Robert Gibson** graduated from Mississippi State University with a Ph.D. in physiology and holds a master's degree in zoology and a bachelor of science degree in general science from the same institution. His primary research interests include the toxicology and behavior of pesticides in aquatic and estuarine environments. Dr. Gibson retired as a director in DuPont's Crop Protection Products Division in Wilmington, Delaware, in 2001. During his 30-year career with DuPont, he held positions in research and development, chemical plant management, and corporate administration (serving as corporate director of safety and health). He was also assistant director of DuPont's Haskell Laboratory for Toxicology and Industrial Medicine. Dr. Gibson is board-certified in toxicology by the American Board of Toxicology and is currently a consultant in toxicology and occupational safety and health. With more than 25 years of experience in toxicology and occupational safety and health, he served for 8 years with the NRC Committee on Review and Evaluation of the Army Chemical Stockpile Disposal Program (Stockpile Committee). He was also a member of the NRC Committee on Evaluation of Chemical Events at Army Chemical Agent Disposal Facilities. In October 2003, Dr. Gibson was appointed U.S. representative to the Scientific Advisory Board of the Organization for the Prohibition of Chemical Weapons.

**Peter R. Griffiths**, professor of analytical chemistry and chair of the Department of Chemistry, University of Idaho, received his B.A. in 1964 and his Ph.D. in 1967, both from Oxford University, and was a postdoctoral fellow at the University of Maryland from 1967 to 1969. He has served previously on the NRC Committee on Testing and Evaluation (T&E) of Standoff Chemical Agent Detectors. Professor Griffiths' research is centered on the application of vibrational spectrometry to the solution of problems of analytical, environmental, and structural chemistry. The current projects that are being worked on by members of his research group include the development of a completely automated open-path FT-IR (OP/FT-IR) spectrometer, investigations into the theory and practice of surface-enhanced infrared absorption, applications of an ultra-rapid-scanning FT-IR spectrometer, and the study of catalytic reactions by diffuse reflection infrared spectrometry. Another project being studied in this laboratory, in collaboration with a small business in Troy, Idaho, Manning Applied Technology, involves the development of a new type of FT-IR spectrometer that currently allows the measurement of complete infrared spectra in 5 milliseconds. In principle, the scan time of this instrument can be reduced to allow spectra to be measured in as little as 1 millisecond.

**James R. Klugh** is currently the technical director and vice president for information technology for Dimensions International, Inc. A retired Army major general, his last military position was as assistant deputy chief of staff for logistics at Headquarters, Department of the Army. A graduate of South Carolina State University with a B.S. in chemistry and mathematics, Mr. Klugh also has an M.S. in administration and management from Shippensburg State College in Pennsylvania. He served as director of the Department of Defense's chemical and biological research, development, and defense programs, and has also developed plans and managed activities in response to chemical, biological, and nuclear incidents. Mr. Klugh established a joint total-asset-visibility program for tracking supply support to all armed forces, including the National Guard and Reserves. This program included the use of best technology solutions in radio-frequency, satellite tracking, and automatic identification equipment. The global technical architecture of tracking and reporting devices established the foundation for in-transit visibility of personnel, equipment, and supplies across the Department of Defense.

**Loren D. Koller** is an independent consultant and former professor and dean of the College of Veterinary Medicine at Oregon State University. His research interests include the toxicologic, pathologic, and immunologic effects of toxic substances and the effect of environmental contaminants on tumor growth and immunity. Dr. Koller is a former member of the NRC Committee on Toxicology and participated on several of its subcommittees, including the Subcommittee on Immunotoxicity and the Subcommittee on Zinc Cadmium Sulfide. He is currently serving on the Institute of Medicine's Committee on the Assessment of Wartime Exposure to Herbicides in Vietnam. He received his D.V.M. from Washington State University and his Ph.D. in pathology from the University of Wisconsin.

**Gary D. Sides**, senior scientist and director of government marketing for GTI Defense, Birmingham, Alabama, has 25 years of experience in the development of automated and manual methods and the manufacture of automated monitoring systems to determine sarin (GB), VX, mustard, and other agents at the current worker protection levels and at the proposed CDC airborne exposure levels. Following the receipt of his Ph.D. in physical chemistry from the University of Florida in 1975, Dr. Sides conducted, and later directed, research, development, testing, and evaluation of automated and manual monitoring systems and accessories for the near-real-time detection of chemical warfare agents. His efforts in this area have included the design, development, and manufacture of ACAMS; the design, development, manufacture, and support of the MINICAMS; and the development of improved DAAMS methods. These three automated and manual methods form the basis of the Army's agent monitoring technology currently used in the non-stockpile and

stockpile programs. His work in air monitoring during the past 25 years has been conducted not only at CMS Research Corporation, which he founded and ran for 12 years, but also at Southern Research Institute, from which he retired in 2003.

**Albert A. Viggiano**, a research chemist with the Space Vehicles Directorate of the Air Force Research Laboratory, graduated from the University of California at Berkeley with a B.Sc. in chemistry (with highest honors) in 1976. He received his Ph.D. in chemical physics from the University of Colorado at Boulder in 1980. Since graduate school, he has been active in the fields of atmospheric ion chemistry and kinetics, specifically in measuring ion molecule reaction rates of interest to atmospheric chemistry. Dr. Viggiano developed a chemical ionization mass spectrometer detection scheme for studying the thermal decomposition of  $N_2O_5$  and was involved in measuring the chemistry that allowed sulfuric acid measurements in the atmosphere to be made. As a postdoctoral fellow in Heidelberg, Germany, he used these measurements to derive the first height profiles of sulfuric acid in the atmosphere and was involved in obtaining and analyzing in situ mass spectrometric data on the ion composition of the stratosphere. Since coming to the Air Force Research Laboratory in 1983, Dr. Viggiano has worked on measurements of ion kinetics related to a number of problems over a broad range of conditions. He has developed a technique that allows the effects of internal energy on the reactivity of gas phase ion molecule reactions to be studied. Using this technique, he has studied the effect of rotational energy on reactivity in more systems than that known collectively elsewhere. He has been instrumental in developing a technique to measure ion molecule reactions at temperatures over 1000 K for the first time. The addition of a supersonic expansion source to the selected ion flow drift tube allows for the measurement of mass selected cluster ions at thermal energy for the first time. A high-pressure turbulent flow tube is the first of its type for studying ion molecule reactions. Dr. Viggiano has authored or co-authored more than

240 papers and book chapters and has given 70 seminars at universities and laboratories and over 230 presentations at scientific meetings. He was lead author of the paper of the year at the Phillips Laboratory in 1993 and spent 2 months at the Max Planck Institut fur Kernphysik working with Frank Arnold under the Air Force Window on Europe program. He won the Loeser Award in 1997 and the Air Force Basic Research Award in 1999.

**David R. Walt**, Robinson Professor of Chemistry at Tufts University, received a B.S. in chemistry from the University of Michigan and a Ph.D. in chemical biology from the State University of New York at Stony Brook. After postdoctoral studies at MIT, he joined the chemistry faculty at Tufts. Dr. Walt served as Chemistry Department chairman from 1989 to 1996. He serves on many government advisory panels and boards and chaired a National Research Council panel on New Measurement Technologies for the Oceans and was a member of the NRC Committee on Waterborne Pathogens and the Committee on Review of Testing and Evaluation Methodology for Biological Point Detectors. He served for 7 years as executive editor of *Applied Biochemistry and Biotechnology* and serves on the editorial advisory board for numerous journals. Dr. Walt is the scientific founder of Illumina, Inc. He has received numerous national and international awards and honors recognizing his work, including a National Science Foundation Special Creativity Award, the Biosensors and Bioelectronics Award, and the Samuel R. Scholes Award in Glass Science. He was elected a fellow of the American Association for the Advancement of Science in 2000. Funding for his work has come from the Department of Energy, National Science Foundation, National Institutes of Health, Office of Naval Research, Defense Advanced Research Projects Agency, and Environmental Protection Agency, as well as numerous foundations and corporations. Dr. Walt has published more than 150 papers, holds more than 30 patents, and has given hundreds of invited scientific presentations.



## Appendix B

### Committee Meetings and Other Activities

#### **WORKSHOP—TECHNOLOGIES FOR CHEMICAL AGENT DETECTION**

**August 24, 2004**  
**Washington, D.C.**

##### *Attendees*

Charles Kolb, Chair, National Research Council (NRC)  
Monitoring Committee  
Margaret Novack, NRC Study Director

#### **FIRST MEETING**

**September 7-8, 2004**  
**Washington, D.C.**

##### *Objectives*

Give National Research Council introduction; complete administrative actions, including committee introductions and composition/balance/bias discussions for members, and committee and report procedures; discuss statement of task with sponsor; receive presentations from U.S. Army and other government agencies relevant to statement of task; discuss draft report outline; discuss project plan and report realization; make writing assignments; confirm objectives, locations, and dates for the next two committee meetings.

##### *Presenters*

David Cullin, Joint Program Executive Office for Chemical and Biological Defense  
Cheryl Maggio, U.S. Army Chemical Materials Agency  
Raj Malhotra, U.S. Army Chemical Materials Agency

Kirkman Phelps, U.S. Army Research, Development, and Engineering Command—Edgewood Chemical Biological Center

Donald Siebenaler, Study Director, Committee on Chemical Demilitarization

Colleen Weese, U.S. Army Center for Health Promotion and Preventive Medicine

#### **SECOND MEETING**

**October 5-6, 2004**  
**Edgewood, Maryland**

##### *Objectives*

Complete composition/balance/bias discussions for members; receive presentations from U.S. Army; discuss draft report outline; develop concept draft; discuss project plan and report realization; make writing assignments; confirm objectives, locations, and dates for the next two committee meetings.

##### *Presenters*

Robert Durgin, Chief, Monitoring Team, Chemical Materials Agency (CMA)

Jeffrey M. Kiley, Monitoring Office, Risk Management Directorate, CMA

Drew A. Lyle, Environment Office, Risk Management Directorate, CMA

Cheryl L. Maggio, Senior Project Engineer, Operations Division, CMA

Robert Schrengost, General Physics Corporation

APPENDIX B

**THIRD MEETING**

**November 22-23, 2004**  
**Washington, D.C.**

*Objectives*

Receive presentations from U.S. Army; discuss draft report outline; develop first full message draft; discuss project plan and report realization; discuss site visit; make writing assignments; confirm objectives, locations, and dates for the next committee meeting.

*Presenters*

Tommy Adams, Pueblo Chemical Agent Destruction Pilot Plant  
David Bradley, Senior Engineer, Science Applications International Corporation  
Robert Durgin, Chief, Monitoring Team, CMA  
Jeffrey M. Kiley, Monitoring Office, Risk Management Directorate, CMA  
Raj Malhotra, U.S. Army Chemical Materials Agency  
Craig Myler, Battelle  
Gregory St. Pierre, Chief, Risk Management Directorate, CMA

**SITE VISIT**

**December 20-22, 2004**  
**Pine Bluff, Arkansas**

*Attendees*

Charles Kolb, Chair, NRC Monitoring Committee  
Gary Sides, Member, NRC Monitoring Committee  
Margaret Novack, NRC Study Director

**FOURTH MEETING**

**January 11-12, 2005**  
**Irvine, California**

*Objectives*

Discuss pre-concurrence draft report; develop concurrence draft; discuss project plan and report realization; make writing assignments, if necessary.

*Presenters*

None

## Appendix C

# Sense of the Senate on Airborne Chemical Agent Monitoring Systems at U.S. Chemical Stockpile Sites

CONGRESSIONAL RECORD  
SENATE  
PAGE S6885  
May 21, 2003

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BUNNING AMENDMENT SA 789

### TEXT OF AMENDMENT

SA 789. Mr. BUNNING submitted an amendment intended to be proposed by him to the bill S. 1050, to authorize for fiscal year 2004 for military activities of the Department of Defense, for military construction, and for defense activities of the Department of Energy, to prescribe personnel strengths for such fiscal year for the Armed Forces, and for other purposes; which was ordered to lie on the table; as follows:

At the end of subtitle D of title X, add the following:

SEC. 1039. SENSE OF SENATE ON DEPLOYMENT OF AIRBORNE CHEMICAL AGENT MONITORING SYSTEMS AT CHEMICAL STOCKPILE DISPOSAL SITES IN THE UNITED STATES.

(a) FINDINGS.—The Senate makes the following findings:

(1) Millions of assembled chemical weapons from rockets, land mines, fuses, explosives, propellants, chemical

agents, shipping and firing tubes, packaging materials, and similar material are stockpiled at chemical agent disposal facilities and depots sites across the United States.

(2) Some of these weapons are filled with nerve agents, such as GB and VX and blister agents such as HD (mustard agent).

(3) Hundreds of thousands of United States citizens live in the vicinity of these chemical weapons stockpile sites and depots.

(4) The airborne chemical agent monitoring systems at these sites are inefficient or outdated compared to newer and advanced technologies on the market.

(b) SENSE OF SENATE.—It is the sense of the Senate that the Secretary of the Army should develop and deploy a program to upgrade the airborne chemical agent monitoring systems at all chemical stockpile disposal sites across the United States in order to achieve the broadest possible protection of the general public, personnel involved in the chemical demilitarization program, and the environment.

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