

Assessment of Agent Monitoring Strategies for the Blue Grass and Pueblo Chemical Agent Destruction Pilot Plants

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In the last 25 years, the U.S. Army has successfully destroyed 90 percent of its approximately 30,000-ton legacy of stockpiled chemical agents. The remaining 10 percent of the nation's stockpile is stored at two continental U.S. depots in Lexington, Kentucky and Pueblo, Colorado. The Army's Assembled Chemical Weapons Alternatives (ACWA) Element is currently constructing the last two demilitarization facilities at these locations, with disposal activities scheduled to start in 2015 and in 2020. This report describes the planned chemical weapons destruction processes to be employed at these demilitarization facilities and analyzes the probable secondary waste streams and planned waste treatment and disposal activities at the plants. It also reviews the potential opportunities emerging from the recent development of ambient ionization mass spectrometric technologies to directly monitor chemical agent contamination levels in real-time (seconds). As detailed in the full report, incorporating these recommended techniques could enhance the safety and effectiveness of current decontamination strategies; however, further evaluations would be needed to effectively deploy these recommended agent monitoring strategies.

Introduction and Background

Although never used, the United States developed and produced a wide range of weapons designed to disperse both nerve and blister chemical agents at lethal concentrations following World War II. These efforts produced a stockpile of 31,496 tons of chemical agents loaded into millions of individual munitions or stored in bulk containers. To date, the U.S. Army's Chemical Materials Agency (CMA) has completed the destruction of the chemical agents and associated munitions stored at six of eight continental U.S. storage sites and on Johnson Atoll, southwest of Hawaii. These efforts have reduced the nation's chemical weapons stockpile by 90 percent.

Congress assigned the job of destroying the final 10 percent of stockpiled chemical weapons at the two remaining continental U.S. storage sites, the Blue Grass Army Depot in Kentucky and the Pueblo Chemical Depot in Colorado, to a U.S. Army Element, the Assembled Chemical Weapons Alternatives (ACWA). The creation of this new program within the Department of Defense occurred after residents near these two storage sites voiced concerns to their congressional representatives regarding the safety and effectiveness of the CMA's incineration-based destruction technology, which has since been used successfully to completely destroy the chemical agents at five of the nine storage sites.

As a result, the two ACWA facilities, which used neutralization (chemical hydrolysis) as the primary agent destruction process, will not have large furnaces to decontaminate or destroy munitions components and to process related secondary waste streams. This constraint has motivated an interest in analytical methods that can quickly and reliably identify and characterize agent-contaminated materials during disposal operations, especially during closure activities when the facilities must be decontaminated before demolition.

Current Methods for Monitoring Contamination

All chemical weapon demilitarization technologies generate large amounts of potentially agent-contaminated secondary wastes, equipment, machinery, and plant structural elements. In order to develop safe decontamination strategies and/or disposal options, contamination levels resulting from agent and energetics destruction processes have to be determined. This includes the structural elements of the plants, which may need to be decontaminated during the course of disposal operations, during agent-changeover breaks in plant operations, and ultimately, as part of plant closure.

Current monitoring methods generally involve vapor-based techniques, both for measuring ambient air agent concentrations and agent contamination of materials, including waste. For the latter, this involves (1) isolating the objects in an enclosure and, (2) after a specified time, measuring vaporized agent concentrations in the headspace of the enclosure containing the material being monitored. In other cases, solvents may be used to extract chemical agent contaminants from wipe samples or waste stream materials, which are then analyzed with chromatographic techniques.

While these approaches—which are planned for use in the two new ACWA plants—are proven effective, they can be time-consuming and indirect as a consequence of their reliance on vapor-phase agent measurements rather than direct detection of surface contamination. However, recent advances in analytical instrumentation suggest that it may be feasible to deploy robust portable instruments that can detect and characterize chemical agent contamination of a wide variety of materials in real time.

Any new monitoring method that could reliably locate and quantify agent contamination may make plant operations and decontamination activities more efficient by enabling faster identification of contamination on equipment, waste materials, and personnel protective equipment, as well as structural materials surfaces (such as aluminum, steel, and concrete.) This approach would potentially reduce the number and/or duration of worker entries in fully suited demilitarization protective ensembles (DPE) during normal plant operations, agent changeover periods, and closure activities; reduce the total amount of secondary waste; expedite waste disposal; and minimize potential worker exposures to agents.

Ambient Mass Spectrometry Methods

The last 5 years have produced very rapid development of ambient ionization mass spectrometric techniques capable of real-time surface and bulk material chemical analyses with little or no sample preparation. This technology is capable of highly sensitive, real-time measurements of relative concentrations of chemical agents adsorbed onto or absorbed into a variety of surfaces and in some porous materials. Further, with appropriate standards for reference, absolute measurements of agent concentrations in ambient air and liquid solutions are feasible. If adopted, these capabilities are anticipated to complement the Army's existing air and vapor headspace monitoring strategies and may improve workplace and environmental safety.

These capabilities are particularly relevant for more efficient and timely characterization of wastes during the agent processing and agent changeover phases of demilitarization operations. For example, the ability to rapidly scan protection gear as workers exit Class A areas, in which they were potentially exposed to chemical agents, could enhance worker safety while greatly reducing the time spent in decontamination and transition. These technologies could also yield significant cost savings by reducing the time required for activities in the plant-decommissioning phase. Finally, the spatial resolution and rapid temporal response might prove to be invaluable assets in providing the capability to track agent vapors back to the source in dealing with any unanticipated agent release events.

Two of the technologies described in the report—desorption electrospray ionization (DESI), first introduced in 2004, and direct analysis in real time (DART), introduced in 2005—have been commercially available for several years and have widespread applications. When compared with existing vapor monitoring measurement strategies, both DART and DESI, as well as a range of variations on each, may be particularly applicable to the detection and quantification of contamination by various chemical agent compounds.

Potential Applications of DART and DESI

While a multitude of other ambient sampling techniques have been described in the last 5 years, DART and DESI are by far the most popular techniques in terms of the range of demonstrated applications, the number of users, and the number of scientific applications. Due to their real-time, spatially resolved capabilities, DART and DESI can directly locate the agent's contamination on solid matrices. With appropriate modifications, DART may also be used to measure trace components in vapor plumes and locate their sources by tracking airborne agent concentration gradients in real time.

In most laboratory mass spectrometric instrumentation, the operator must bring the sample to the instrument in order to maximize ion transport. However, with the new sampling technologies, it is possible for the instrument to be brought to the sample, facilitating the use of cart-mounted or even personnel-carried instruments capable of identifying localized regions of agent contamination on surfaces. In addition, even though DART and DESI are designed to detect surface contaminants, it might be possible to further develop methods of operation—or combine methods with a second ambient ion source for vapor-phase detection—to produce a single portable instrument able to perform rapid vapor and surface analyses.

Based on detailed analyses of potential waste stream scenarios, as evaluated in the full report, the most fitting platform configuration most likely consists of a cart-mounted or handheld mass spectrometer equipped with a modified interface to accommodate a special remote sampling wand, a surface ambient ionization source combined with a vapor ambient ionization source, and any sampling accessories. These systems, when backed by an uninterrupted power supply, would allow portability between different rooms or site areas without breaking vacuum. Careful attention to instrument shielding and sampling wand design and implementation can reduce the possibility of agent contamination during instrument use.

While both DART and DESI have demonstrated excellent sensitivity for detecting chemical agents in liquids and on a wide range of surfaces, DART is the recommended ionization method based on its lower dispersion of target species, utilization of a gas rather than a liquid as the working medium, and ability to efficiently ionize and detect trace levels of species in the gas phase. A DESI system with a cover shield to intercept dispersed contaminants may also be applicable. The use of instrument shields to minimize agent contamination could be investigated during instrument test and evaluation activities.

However, it is important to note some of the limitations associated with ambient ionization mass spectrometry techniques—these include the potential for instrumental contamination by dispersed agent, signal saturation (owing to high sensitivity of the measurements), and a lack of regulatory standards for agent surface concentration measurements. The use of DART, DESI, or related new analytical methodologies for surface area measurements at the Pueblo Chemical Agent Destruction Pilot Plant or the Blue Grass Chemical Agent Destruction Pilot Plant requires that the quality of measurements be determined and related calibration studies be performed for relevant matrices. In addition, ACWA staff should have access to sufficient statistical expertise to develop effective sampling protocols for any application of ambient ionization monitoring. Once the resulting expert sampling protocols have been developed, ACWA headquarters monitoring staff or their contractors should then proceed to develop detailed standard operating procedures to guide monitoring technicians.

In summary, the combination of real-time measurements with multi-state (gases, liquids, and solids) analytical capability suggests that newer instruments that incorporate remote sampling capabilities deserve serious consideration as supplements to the current agent monitoring instruments. Based on these capabilities, and on the potential measurement strategies reviewed in the report, these instruments have the potential to enhance workplace safety, improve operational efficiency, and accelerate decontamination activities during both operational and closure activities at the two facilities. ACWA should carefully evaluate the capabilities of portable ambient ion mass spectrometry and its potential to provide faster and more accurate characterization of chemical agent contamination, as detailed in the report, and determine if these likely benefits justify the effort and investment required to specify, acquire, and deploy suitable implementations of this technology.

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