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Appendix C. Collection of Samples for Chemical Agent Analysis

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Appendix C. Collection of Samples for Chemical Agent Analysis

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C.1. Purpose

This chapter describes procedures for the collection and analysis of samples of various matrices for the purpose of determining the presence of chemical agents in a civilian setting. This appendix is intended to provide the reader with sufficient information to make informed decisions about the sampling and analysis process and to suggest analytical strategies that might be implemented by the scientists performing sampling and analysis. This appendix is *not* intended to be used as a standard operating procedure to provide detailed instructions as to how trained scientists should handle samples.

Chemical agents can be classified by their physical and chemical properties. Table 1 lists the chemical agents considered by this report. In selecting sampling and analysis methods, we have considered procedures proposed by the Organisation for Prohibition of Chemical Weapons (OPCW), the U. S. Environmental Protection Agency (EPA), and peer-reviewed scientific literature. EPA analytical methods are good resources describing issues of quality assurance with respect to chain-of-custody, sample handling, and quality control requirements.

Table 1. Chemical agents considered in this report.

Agent Class	Agent	Symbol	Persistency	Rate of Action
Nerve	Tabun	GA	Low	Very rapid
	Sarin	GB	Low	Very rapid
	Soman	GD	Moderate	Very rapid
	VX	VX	Very high	Rapid
Blister	Sulfur mustard	H, HD	Very high	Delayed
Choking	Phosgene	CG	Low	Delayed
Blood	Hydrogen cyanide	AC	Low	Rapid
	Cyanogen chloride	CK	Low	Rapid

C.2. Sampling Plan

A sampling event begins with the creation of a sampling plan, which defines what problem is to be solved (*e.g.* certifying a building safe for re-occupancy) and the information required in the process. A good sampling plan typically documents project objectives, data quality objectives, sample collection requirements, analysis and testing requirements, quality control requirements, required project documentation, and identification of the organizations conducting laboratory and field operations (EPA 1997). It is critical to develop and adhere to a thorough sampling plan so that the data generated are scientifically and legally defensible and so that the analytical results are readily accepted by various stakeholders. Detailed information regarding the creation of a sampling plan can be found in Appendix I of this document.

C.2.1. Sample Control and Documentation

It is necessary to document sample collection and to maintain sample control so that legally and scientifically defensible data are produced. The purpose of sample control is to unambiguously connect the origin, history, and analytical test results of each sample. Various procedures for sample control have been discussed for environmental (EPA 1997) and Chemical Weapons Convention treaty verification (Rautio, 1993) applications.

Sample control is conducted through assigning a unique identifier, most often a number or a bar code, to each sample. This sample identifier is placed on sample bottles, is written in field and laboratory notebooks (which are also controlled and have their own unique names/numbers so that they can be unambiguously identified), and is recorded on test result reports. Logbook entries should describe the sampling event as accurately as possible and include the date and time of sampling, the method of sample collection, condition of the site relevant to sample validity when applicable, results of associated field measurements (such as on-site meteorological data) and calibration information pertaining to the field instruments used, and the name of the field personnel performing the work.

A documented chain-of-custody (COC), or historical record, is also established and follows each sample through collection, transport, analysis, and final data reporting. In addition to a sample's unique identifier, information provided by COC might include the identifier of the field logbook that documents the sampling event, date and time of sample collection, the sample matrix and container, the sampler's name, the project name, the name of the analytical laboratory providing services, the required laboratory tests and turn-around times, and any additional instruction to the laboratory. The date and time the sample is relinquished and by whom and the date and time it is received by the carrier or analyst is noted on the COC. Samples

must be under the direct control of the individual signing for the samples on the COC form at all times. This includes storing the samples in a locked, secure facility under the control of the COC signatory.

C.2.2. Transport of Samples

As described below (see section C.3), a number of different samples are likely to be collected during the decontamination phase responding to a chemical attack. Precautions need to be taken in moving samples from the site of collection to the site of analysis in order to protect the health of individuals exposed to the samples during transport and in order to preserve sample integrity. Chain of custody issues with sample transport were previously described (see section C.2.1). In this section, precautions necessary for health protection of individuals potentially exposed to the samples during transport and preservation of samples during transport are described.

Samples collected at the site of a chemical agent attack may themselves present a health hazard and their transport should be treated as transport of a hazardous material. Samples will either be transported to an onsite location for analysis or be taken to an offsite laboratory specializing in the detection of trace concentrations of chemical agents. Transport of samples within the response site boundaries should follow all site requirements for contamination control. For example, contamination control may require additional external packaging at the boundaries of specific contamination zones. Procedures and facilities for this additional packaging should be in-place prior to the transport of samples. Composition of packing materials should be selected so that it forms a barrier to permeation of contaminant materials and their vapors. The outside of packages containing samples should be screened for contamination by the use of portable field monitors. For example, photoionization monitors can be used to detect the presence of organophosphate chemical agents.

Samples destined to offsite laboratories for analysis may fall under hazardous material transportation regulations. Note that there are only a few laboratories in the United States that are capable of conducting analyses of chemical warfare agents (CWAs) and, thus, to which samples containing CWAs could be sent. Within the United States, samples might be transported by highway, air, rail, and/or water. The transport of hazardous materials/environmental samples is governed by regulations that are based on the mode of sample transport. For example, highway transportation of hazardous materials is governed by Department of Transportation 49 Code of Federal Regulations (CFR), civilian air transport is governed by International Air Transport Association (IATA) and International Civil Air

Organization (ICAO) Technical Instructions, military air transport is governed by Air Force Joint Manual 24-404 (AFJM 24-404), and water transportation is governed by International Maritime Dangerous Goods (IMDG) Code. Sample packaging and labeling will need to conform to the regulations under which the shipping company operates. However, in a federally declared State of Emergency, there is precedent for the U.S. Secretary of Transportation to waive some regulatory requirements. In addition, both the military and the U.S. Federal Bureau of Investigation have special authority and provisions for shipping hazardous materials.

Shipping samples that are considered to be neat agents will be difficult, if not impossible. If samples can be designated as environmental samples, which typically have low or negligible concentrations of hazardous constituents (as would be the case after decontamination procedures have been applied), sampling shipping is considerably easier. The previously described regulations will specify appropriate sample shipping and packaging protocols. There are also recommended procedures for packaging samples collected by the Organisation for Prohibition of Chemical Weapons (OPCW) to verify the Chemical Weapons Convention treaty (Rautio 1993). Neat agent and potentially-highly contaminated materials are packaged in a sampling container, placed in a stainless steel secondary container with absorbent material, and placed in a tertiary stainless steel, pressure-tight container (lid sealed with nuts and bolts) before being placed in a shipping crate (see Rautio 1993, Recommended Operating Procedure GS 2). All containers are also sealed with tamper-indicating tape or seals. Environmental samples are packaged in a comparable manner, with the exception that, because the concentration of agent residues are expected to be below those associated with extremely adverse health effects, tertiary containment is not necessary (see Rautio 1993, Recommended Operating Procedure GS 3). Once packaged, the outside of the sample container could be checked for contamination, as previously described. During transport, samples must be accompanied by a shipping document (*ie.* a Bill of Lading, Declaration for Dangerous Goods, Airbill, or Manifest) completed and signed by a properly trained (per Defense Transportation Regulations, DOD 4500.9) individual.

Actions should be taken to assure that collected samples accurately reflect conditions at the location and time they were obtained in the contamination zone. Preservation of the integrity of samples requires actions to prevent loss of material from the sample and to prevent contamination of the sample. Loss of material from the sample can occur through direct contact packing materials or through outgassing of vapors from the sample. Often, environmental samples are shipped in coolers packed with ice to keep the temperature of the sample sufficiently low (4-7°C) to minimize volatilization of analytes.

C.3. Sample Collection

Many different types of samples may be needed to characterize, confirm success of decontamination, and to clear facilities for reuse. This is because many different media may be contaminated and because no single method detects all chemical agents. The type of sample collected, therefore, will be determined by the matrices or media to be sampled and the analytical methods to be used to assess the sample. This section describes sample collection methods for air, surfaces, solids (including chips, bulk materials, and soils), vegetation, and liquids. There are distinct advantages and disadvantages in the types of media sampling that need to be considered in selecting sample methods. Table 2 summarizes the advantages and disadvantages of collecting various sample types.

Several publications describe sample collection methods to detect contaminants (EPA 2002, ASTM 2004). These are excellent references; however, they focus on collecting large samples, in outdoor settings, for purposes dissimilar to decontamination and reuse of facilities. Despite the differences in analytical objectives, these references provide some useful sampling guidelines. For example, in any sampling activity, care should be taken to ensure collection equipment is clean between samples to avoid cross-contamination of samples. Similarly, sample location identification, and sample container markings need to be complete and easy-to-interpret to support chain of custody requirements.

Table 2. Types of samples that can be analyzed for the presence of chemical warfare agents (CWA).

Sample Type	Advantages	Disadvantages
Air	<ul style="list-style-type: none"> - can detect CWA in a large, general area - provides direct information on inhalation hazard - can obtain real-time results with appropriate instruments 	<ul style="list-style-type: none"> - difficult to pinpoint precise areas requiring decontamination or re-decontamination - results will not provide information on contact or ingestion hazards
Surface Samples/Swipes	<ul style="list-style-type: none"> - used to rapidly and easily sample surfaces - can collect many samples - provide information for contact hazard analysis 	<ul style="list-style-type: none"> - sorbed CWA not always readily detected (especially on porous surfaces) - results cannot be used to predict inhalation hazard
Chips/ bulk sample	<ul style="list-style-type: none"> - can detect presence of sorbed CWA - provides more definitive proof of presence or absence of CWA 	<ul style="list-style-type: none"> - destructive analysis, requires partial destruction of surface being sampled - complex extraction procedures, with potential for multiple interferences - limited number of samples can be collected - results cannot be used to predict inhalation hazard
Environmental (water, soil, vegetation, liquids)	<ul style="list-style-type: none"> - can collect many samples - can detect presence of sorbed CWA - can use results to provide contact and ingestion hazard analysis - can use results to delineate extent of contamination in outdoor scenarios 	<ul style="list-style-type: none"> - complex extraction procedures, with potential for multiple interferences - results cannot be used to predict inhalation hazard

Air Sample Collection

Air sampling of the general environment and of potentially degassing surfaces provides the most direct evidence of the presence of a CWA. In addition, the air is the pathway of highest concern with respect to human exposure and provides the best quantitative basis to determine risk to humans. However, air sample results do not provide contact or ingestion hazard information. In addition, air sampling is less useful for determining the precise location of CWA contamination to guide decontamination activities.

Air sampling can be conducted on-site and air samples are commonly used for laboratory methods which have much greater sensitivity. High-volume air samplers and chemical agent monitors (CAMs) are the most common on-site sampling tools. High-volume air samplers can sample over a large area to determine the presence of CWA but cannot determine the specific location of contamination. Small, hand-held chemical agent monitors (CAMs), can rapidly monitor smaller areas.

Surface Sample Collection

Surface samples are used to determine the presence of CWA and to evaluate contact hazard. This method can be used to rapidly determine the contamination extent and decontamination efficacy. Surface sampling may not detect low concentration of sorbed CWA that may still present an inhalation hazard. In addition, sample results do not determine the potential inhalation hazard from the results of surface samples.

Swipe samples are the most common surface contamination sample collection method. Clean cotton swabs or pads are moistened with a solvent (e.g., methylene chloride or acetonitrile) and then wiped over the area of interest. Forceps or a hemostat can be used to hold the swipe to prevent direct contact by the worker and to reduce contamination of the workers protective clothing (e.g., glove). The swipe is then placed in a clean glass vial and sealed for transport to the analytical laboratory. One unusual swipe sample collection method is for workers to use their booties (shoe coverings) as swipes along the floor to assist in determining the general presence of CWA on floors.

Solid Sample Collection (Chip or Bulk Sampling)

Collection and analysis of pieces of solid materials (e.g., pieces of walls, floors, carpeting, personal protective equipment) allow for the detection of sorbed CWAs. These samples can more definitively determine the presence of CWA. Chip/bulk sampling may also provide evidence of decontamination verification. The heterogeneity among samples and the characteristics of the material can interfere with the chemical analysis and reduce the reliability of the analysis results. As an example, concrete is an alkaline matrix that promotes rapid degradation of most

CWAs. Because the CWA is sorbed into the material, analytical results do not provide either a direct measure of contact or inhalation hazard.

Pieces of the contaminated surface are chipped or cut, removed, and placed and sealed in clean glass containers and transported to the laboratory for analysis. The sample is further ground and extracted with an appropriate solvent, and the resulting extract is analyzed for the presence of CWA. The destructive sampling collection process and lengthy laboratory extraction time limits the number of samples that can be collected.

Soil, Vegetation, and Liquid Sample Collection

Soils, vegetation, and liquids are special types of solid samples that are relatively easy to collect. Similar to other types of bulk samples, the potential for signal interference is large and laboratory sample handling (extraction and analysis) is slow. In addition, it is not possible to translate the results of the analysis into a inhalation hazard.

Soil samples can be collected using scoops (spatulas, shovels, pans), coring devices, or sweeping devices. The soil sample should be placed in a clean glass bottle. At the laboratory, the sample should be thoroughly mixed (homogenized) so that the sample has not fractionated based on soil particle size or texture.

Vegetation can be clipped using shears or vegetation cutters. Both woody material and leaf material should be collected separately because sorption by CWAs will likely be different because of orientation of surfaces and differences in permeability.

Water samples can be collected using vials, syringes, teflon tubing, bailers, dippers, etc. (EPA 2002). The choice of sampling equipment will depend of the environment in which the sample is being collected. Syringes may be most appropriate for small puddles, where as bailers or pumps with Teflon tubing best used for deeper water sources.

C.4. Real-time Chemical Agent Monitoring for Initial Phase of Decontamination

Instrumentation for the detection of chemical warfare agents (CWA) during the decontamination phase of a restoration project should be able to make real-time measurements and be portable. We have summarized available technologies for the detection of chemical agents in a separate document/appendix ([refer to “Review of Available Instruments” compiled August 2005](#)). In addition, the ideal instrument should be able to detect the agent(s) of interest at levels below the Short Term Exposure Limits (STEL). If possible, it is preferred to have the ability to detect contaminants at the lower Acute Exposure Guidelines Levels (AEGL). These, and other, health-based guidance values have been summarized in [Section X](#) of this

document (tables of these values will probably be included in the document from the Guidelines Group – ref?). Based on the previously listed criteria and the fact that these instruments provide sensitive and selective detection of CWAs, we recommend that the best instruments for real-time CWA detection during decontamination are the flame photometric detector (FPD), ion mobility spectrometer (IMS), and mass spectrometer (MS); see Table 3.

Table 3. Recommended instrumentation for the real-time detection of CWAs.

Instrumentation	Advantages	Limitations	Sample Matrices
FPD	Portable, low limits-of-detection	Some false positives	Liquids ^a , gas
IMS	Portable, low limits-of-detection, rapid analysis	Some false positives	Solids ^b , gas
MS	Specific identification, low limits-of-detection, rapid analysis	Large footprint, usually in fixed-base or mobile labs	Solids, liquids ^a , gas ^c

^a Liquid samples may include solvent extracts of surface swipes.

^b Solid samples in IMS are generally surface swipes (can include liquids from surfaces) from which the compound vapors are extracted and analyzed.

^c Gas samples may include pre-concentration on sorbent materials and subsequent desorption.

While the above detectors will respond to low concentrations of CWAs, all of the instrumentation can also respond to other environmental contaminants, thus producing a false positive detection of a CWA. IMS yields false positive responses from interferences such as cleaning compounds containing ammonia, N,N-diethylaminoethanol, and latex paint fumes. FPD will give false positive responses from any non-CWA containing phosphorus and sulfur, as well as gasoline vapors in >1% concentrations and smokes. These detection technologies can be combined with an orthogonal technique such as fast gas chromatography (GC) to significantly minimize or eliminate these interference problems. GC/FPD and GC/MS are standard, commercially-available technologies; however, we know of no vendors who are currently producing GC/IMS instruments. (We should probably mention this somewhere as a technology gap which needs filling –need to establish if Smiths Detection still makes this instrument and, if not, modify the “Review of Available

Instruments” accordingly.) MS is the most reliable detector for CWA, both quantitatively and qualitatively. MS hardware is generally considered to be fixed-base instrumentation – however, several portable mass spectrometers are commercially available. Table 4 shows the manufacturers of the selected technologies. Details of instrumentation from the representative manufacturers can be found in previous Tables (refer to “Review of Available Instruments”).

Table 4. Vendors of portable FPD, IMS, and MS systems.

Detector	FPD	Portable GC-FPD	IMS	Portable MS and GC/MS
Vendor	ProEngin	OI Analytical	Bruker-Daltonics Draeger Enviro-nics General Dynamics Smith’s Detection	Bruker-Daltonics Constellation Technologies Corp. Griffin Analytical Technologies Inficon

There are several technologies that are capable of providing real-time detection of CWAs at low concentrations. If these technologies are to be used in decontamination situations, they must be checked for false positives responses against the decontamination agents and any other common chemicals used in the decontamination process/area.

C.5. Lab-based Analysis Methods for Late-stage Decontamination and Clearance

Analysis of collected samples will be the bottleneck of the remediation process. The laboratory-based analysis of samples will be time-consuming because of the great number of samples that will require analysis (>10,000) and the significant amount of time that will be needed to prepare the samples so that trace amounts of analytes can be successfully measured in the presence of matrix interferences. If a chemical contaminant is identified as a chemical warfare agent (*ie.* a compound listed under Schedule 1A of the Chemical Weapons Convention), there are only half a dozen laboratories in the United States that would be able to analyze the samples and work with authentic standards of the agent.

In addition, there are no standardized, validated methods for the quantitative determination of trace (part-per-billion, or lesser, concentrations) chemical warfare agents in environmental matrices. During the clearance phase of the remediation process, it will be important to be able to accurately determine such low concentrations of analytes. While the Organisation for Prohibition of Chemical Weapons (OPCW), whose mission is to implement the provisions of the Chemical Weapons Convention, does promote methods for the determination of chemical warfare agents and related compounds, these methods are targeted at detecting the presence of analytes at concentrations greater than a part-per-million in various matrices. OPCW methods are also only qualitative (not quantitative) in nature. The U.S. Environmental Protection Agency (EPA) has proposed that laboratories use standard analysis protocols in the event of a National emergency (EPA 2004). The selected methods are currently in use by government agencies, such as EPA, National Institute of Occupational Safety and Health (NIOSH), Occupational Safety and Health Administration (OSHA), ASTM International, and the Centers for Disease Control (CDC), that monitor human exposure to environmental contaminants. Such methods were developed and validated to measure a multitude of preselected environmental contaminants of anthropogenic origin. These methods were not developed to determine compounds such as chemical warfare agents. However, because standardized methods for the determination of trace concentrations of chemical warfare agents are lacking, these protocols have been suggested for use in chemical agent determination based on the known properties of chemical agents only and HAVE NOT BEEN VALIDATED by experiments, such as method detection limit and stability studies, with selected agents. Thus, laboratories that might be called on to measure the concentrations of agents in air, solid samples, and water will have to invest time researching the chemical literature and developing analytical and quality assurance measures prior to analyzing real samples.

Tables 5, 6, and 7 list methods that could be used for the determination of analytes of interest in air (Table 5), many types of solid samples, including swipes (Table 6), and

water (Table 7). These methods represent techniques that have been proposed for use by the EPA in the event of a national emergency as well as methods that have been published in the chemical literature. Several methods are listed as “standard methods” because they are routinely used by government agencies to measure analytes of environmental significance. We emphasize that these methods, in most cases, have not been validated for use with chemical agents such as sarin, soman, sulfur mustard, tabun, and VX (*ie.* method performance, with respect to sample storage, analyte extraction, and analyte detection for these analytes, has not been tested). While the EPA endorses sample storage by refrigeration, it might be more appropriate to store solid samples, including air samples collected on a solid sorbent, at a freezing temperature of -20°C. Tables 5, 6, and 7 also include methods published in the scientific literature; although these methods were found to perform well for their authors’ studies, they have not necessarily been successfully implemented by other laboratories. Several relevant health guideline levels are listed in Tables 5, 6, and 7. These guidelines represent concentrations below which remediation efforts strive to achieve and that analytical methods must be capable of accurately and precisely measuring.

In selecting an appropriate analytical method, the most crucial factors will be to choose a method that provides sufficient detection limits to address questions of human safety and that uses technologies that will provide accurate, reproducible, and scientifically and legally defensible data. As can be seen from the information in Tables 5, 6, and 7, there are many options available to the analyst. In general, analysis strategies coupling a chromatographic separation prior to analyte detection (for example, gas chromatography coupled with flame photometric detection, atomic emission detection, or mass spectrometry and liquid chromatography coupled with mass spectrometry) will provide the most reliable data. The equipment to perform such analyses is readily accessible in most good contract laboratories. In addition, the quality assurance measures (*eg.* method detection limit studies, precision and accuracy studies, analysis of blank and duplicate samples, *etc.*) routinely used by all good contract laboratories will assure the production of defensible data.

Tables 5, 6, and 7 contain methods used for the determination of selected agents in various matrices. In addition to monitoring the agents themselves, it might be important to monitor the degradation products of selected agents as part of the decontamination/clearance process. Many of the methods previously cited can also be used to detect agent degradation products. For example, liquid chromatography/mass spectrometry can be used to determine VX degradation products (Love 2004) and sulfur mustard degradation products (Creasy 1999). Various chemical reactions to form volatile derivatives of agent degradation products followed by analysis by gas chromatography/mass spectrometry or gas chromatography/flame photometric detection is another strategy that can be successfully used to detect agent degradation products (Creasy 1999, Purdon 1989, Naomi 2002, Black 2003).

Table 5. Air analysis methods for characterization and clearance sampling.					
Analyte (exposure limits)	Standard Method	Sampling Method	Sample Storage	Determination	Ref
Cyanogen chloride (STEL/WPL ceiling = 0.6 mg/m ³ or 0.2 ppmv)	EPA Method TO-15 for preparation; method not validated	Air collected in Summa canister	Ambient temperature for up to 14 days	GC/MS; typical d.l. for VOCs = 0.5 ppbv	EPA 2004
Cyanogen chloride (STEL/WPL ceiling = 0.6 mg/m ³ or 0.2 ppmv)		Might be possible to draw air through basic solution and measure cyanogen chloride as cyanide per NIOSH Method 6010			
Hydrogen cyanide (AEGL _{8-24 hr} = 0.37 mg/m ³ and NIOSH STEL = 5 mg/m ³)	NIOSH Method 6010	2-90 L air, at 0.05-0.2 L/min, drawn through a solid sorbent tube containing lime soda	Ambient temperature for up to 14 days	Sorbent tube extracted with water; sample extract derivatized and analyzed by spectrophotometry; d.l. = 3 mg/m ³	EPA 2004
Phosgene (NIOSH WPL = 0.4 mg/m ³ and NIOSH STEL = 0.82 mg/m ³)	EPA Method TO-6	≤ 50 L air, at rate ≤ 1 L/min, drawn through an impinger containing 10 mL aniline solution	Aniline solution transferred to vial and refrigerated until analysis	Sample prepared and carbanilide analyzed by LC/UV; method d.l. = 4 x 10 ⁻⁴ mg/m ³	EPA 2004
Phosgene (NIOSH WPL = 0.4 mg/m ³ and NIOSH STEL = 0.82 mg/m ³)		Air, at a rate of 1 L/min, drawn through an impinger containing a solution of tryptamine		Tryptamine derivative detected by LC/fluorescence; d.l. = 0.04 mg/m ³	Black 2003
Sarin (AEGL _{8-24 hr} = 3 x 10 ⁻⁴ mg/m ³ and STEL = 1 x 10 ⁻⁴ mg/m ³ and WPL = 3 x 10 ⁻⁵ mg/m ³)	EPA Method TO-13A; method not validated	300 m ³ air sampled on Tenax, XAD-2, or PUF sorbent	Ambient temperature for up to 30 days	Sorbent Soxhlet extracted and extract analyzed by GC/MS; d.l. = 10-1000 pg	EPA 2004
Sarin (AEGL _{8-24 hr} = 3 x 10 ⁻⁴ mg/m ³ and STEL = 1 x 10 ⁻⁴ mg/m ³ and WPL = 3 x 10 ⁻⁵ mg/m ³)		4800 L air sampled at 20 L/min for 4 hr with charcoal canister to provide a diesel exhaust matrix into which sarin was spiked to simulate		Charcoal extracted with dichloromethane and concentrated; extract analyzed by GC/MS/MS; <i>estimated</i> d.l. = 70 pg sarin	D'Agostino 1990

Table 5. Air analysis methods for characterization and clearance sampling.					
Analyte (exposure limits)	Standard Method	Sampling Method	Sample Storage	Determination	Ref
		collection of this agent		in an extract that represented $5 \times 10^{-4} \text{ m}^3$ of diesel exhaust air; assuming 100% recovery of analyte from a charcoal canister, this would correspond to an <i>estimated</i> d.l. = $1.4 \times 10^{-4} \text{ mg/m}^3$	
Sarin (AEGL _{8-24 hr} = $3 \times 10^{-4} \text{ mg/m}^3$ and STEL = $1 \times 10^{-4} \text{ mg/m}^3$ and WPL = $3 \times 10^{-5} \text{ mg/m}^3$)		Air sampled for 5 min with SPME fiber		Detection of $1 \times 10^{-1} \text{ mg/m}^3$ could be obtained with GC/MS	Schneider 2001
Soman (AEGL _{8-24 hr} = $2 \times 10^{-4} \text{ mg/m}^3$ and STEL = $5 \times 10^{-5} \text{ mg/m}^3$ and WPL = $3 \times 10^{-5} \text{ mg/m}^3$)	EPA Method TO-13A; method not validated	300 m ³ air sampled on Tenax, XAD-2, or PUF sorbent	Ambient temperature for up to 30 days	Sorbent Soxhlet extracted and extract analyzed by GC/MS; d.l. = 10-1000 pg	EPA 2004
Soman (AEGL _{8-24 hr} = $2 \times 10^{-4} \text{ mg/m}^3$ and STEL = $5 \times 10^{-5} \text{ mg/m}^3$ and WPL = $3 \times 10^{-5} \text{ mg/m}^3$)		4800 L air sampled at 20 L/min for 4 hr with charcoal canister to provide a diesel exhaust matrix into which soman was spiked to simulate collection of this agent		Charcoal extracted with dichloromethane and concentrated; extract analyzed by GC/MS/MS; <i>estimated</i> d.l. = 60 pg soman in an extract that represented $5 \times 10^{-4} \text{ m}^3$ of diesel exhaust air; assuming 100% recovery of analyte from a charcoal canister, this would correspond to an <i>estimated</i> d.l. = $1.2 \times 10^{-4} \text{ mg/m}^3$	D'Agostino 1990
Sulfur Mustard (AEGL _{8-24 hr} = 3×10^{-3})	EPA Method TO-13A; method not	300 m ³ air sampled on Tenax, XAD-2, or PUF	Ambient temperature for up to 30 days	Sorbent Soxhlet extracted and extract analyzed by	EPA 2004

Table 5. Air analysis methods for characterization and clearance sampling.					
Analyte (exposure limits)	Standard Method	Sampling Method	Sample Storage	Determination	Ref
mg/m ³ and STEL = 3 x 10 ⁻³ mg/m ³ and WPL = 4 x 10 ⁻⁴ mg/m ³)	validated	sorbent		GC/MS; d.l. = 10-1000 pg	
Sulfur Mustard (AEGL _{8-24 hr} = 3 x 10 ⁻³ mg/m ³ and STEL = 3 x 10 ⁻³ mg/m ³ and WPL = 4 x 10 ⁻⁴ mg/m ³)		4800 L air sampled at 20 L/min for 4 hr with charcoal canister to provide a diesel exhaust matrix into which sulfur mustard was spiked to simulate collection of this agent		Charcoal extracted with dichloromethane and concentrated; extract analyzed by GC/MS/MS; <i>estimated</i> d.l. = 30 pg sulfur mustard in an extract that represented 5 x 10 ⁻⁴ m ³ of diesel exhaust air; assuming 100% recovery of analyte from a charcoal canister, this would correspond to an <i>estimated</i> d.l. = 6.0 x 10 ⁻⁵ mg/m ³	D'Agostino 1990
Tabun (AEGL _{8-24 hr} = 3 x 10 ⁻⁴ mg/m ³ and STEL = 1 x 10 ⁻⁴ mg/m ³ and WPL = 3 x 10 ⁻⁵ mg/m ³)	EPA Method TO-13A; method not validated	300 m ³ air sampled on Tenax, XAD-2, or PUF sorbent	Ambient temperature for up to 30 days	Sorbent Soxhlet extracted and extract analyzed by GC/MS; d.l. = 10-1000 pg	EPA 2004
VX (AEGL _{8-24 hr} = 2.4 x 10 ⁻⁵ mg/m ³ and STEL = 1 x 10 ⁻⁵ mg/m ³ and WPL = 1 x 10 ⁻⁶ mg/m ³)	EPA Method TO-13A; method not validated	300 m ³ air sampled on Tenax, XAD-2, or PUF sorbent	Ambient temperature for up to 30 days	Sorbent Soxhlet extracted and extract analyzed by GC/MS; d.l. = 10-1000 pg	EPA 2004
VX (AEGL _{8-24 hr} = 2.4 x 10 ⁻⁵ mg/m ³ and STEL = 1 x 10 ⁻⁵ mg/m ³ and WPL = 1 x 10 ⁻⁶ mg/m ³)		Air sampled at either 4 L/min or 1.5 L/min (dependent on tube i.d.) through a felt pad impregnated with silver fluoride; typical sampling conditions were 1 L/min for 2 hrs, affording a 120 L air		Contents of sorbent tube thermally desorbed into GC/FPD; VX at 2 x 10 ⁻⁶ mg/m ³ could be detected if no interferences present	Fowler 1989

Table 5. Air analysis methods for characterization and clearance sampling.

Analyte (exposure limits)	Standard Method	Sampling Method	Sample Storage	Determination	Ref
		sample; resulting derivative collected on Chromosorb 106			

Abbreviations used in Table 5.

AEGL_{8-24 hr} – Acute Exposure Guidelines; these values have been extrapolated for 24 hour exposure from AEGL-1_{8 hr} values for the purpose of this report; d.l. – detection limit; EPA – United States Environmental Protection Agency; GC/FPD – gas chromatography coupled with flame photometric detection; GC/MS – gas chromatography coupled with mass spectrometry; GC/MS/MS – gas chromatography coupled with tandem mass spectrometry; LC/fluorescence – liquid chromatography coupled with fluorescence detection; LC/UV – liquid chromatography coupled with ultraviolet detection; NIOSH – National Institute for Occupational Safety and Health (United States); ppbv – part-per-billion volume; ppmv – part-per-million volume; PUF – polyurethane foam; SPME – solid phase microextraction; STEL – Short Term Exposure Limit; VOC – volatile organic compound; WPL – Worker Population Limit

Table 6. Characterization and clearance analysis methods for use with solid samples, including swipes. NEED TO INCORPORATE SURFACE GUIDELINE LEVELS WHEN AVAILABLE FROM GUIDELINES GROUP.					
Analyte (exposure limits)	Standard Method	Sample Preparation Method	Sample Storage	Analysis	Ref
Cyanogen chloride				Because CK is a gas at $T \geq 56.8^{\circ}\text{F}$ (13.8°C), surface/solid contamination might not be of great concern.	
Cyanogen chloride	EPA Method 5035A for sample preparation; EPA Method 8260B for determination; method not validated	5 g sample placed in vial and subjected to closed-system purge and trap process in which analytes are collected on a sorbent	EPA Method 5035A lists several storage options; the simplest is storage at $< -7^{\circ}\text{C}$ for up to two weeks	Analytes collected on solid sorbent, removed by thermal desorption, and transferred to GC/MS; 0.5 $\mu\text{g}/\text{kg}$ amounts of VOC typically detected	EPA 2004
Hydrogen cyanide				Because AC is a gas at $T \geq 78^{\circ}\text{F}$ (26°C), surface/solid contamination might not be of great concern.	EPA 2004
Phosgene				Because phosgene is a gas at $T \geq 47^{\circ}\text{F}$ (8.2°C), surface/solid contamination might not be of concern	
Phosgene	EPA Method 5035A for sample preparation; EPA Method 8260B for determination; method not validated	5 g sample placed in vial and subjected to closed-system purge and trap process in which analytes are collected on a sorbent	EPA Method 5035A lists several storage options; the simplest is storage at $< -7^{\circ}\text{C}$ for up to two weeks	Analytes collected on solid sorbent, removed by thermal desorption, and transferred to GC/MS; 0.5 $\mu\text{g}/\text{kg}$ amounts of VOC typically detected	EPA 2004
Sarin (HBESL _{ind} = 41 mg/kg)	EPA Method 3541 for sample preparation; EPA Method 8270D for determination; method not validated	10 g sample processed by automated Soxhlet extraction	Store at 4°C for up to two weeks ^{EPA 1996}	GC/MS; d.l. $\sim 0.7\text{-}3$ mg/kg	EPA 2004
Sarin (HBESL _{ind} = 41 mg/kg)	EPA Method 3545A for sample preparation; EPA Method 8270D for	10-30 g sample processed by pressurized fluid extraction	Store at 4°C for up to two weeks ^{EPA 1996}	GC/MS; d.l. $\sim 0.7\text{-}3$ mg/kg	EPA 2004

Table 6. Characterization and clearance analysis methods for use with solid samples, including swipes. **NEED TO INCORPORATE SURFACE GUIDELINE LEVELS WHEN AVAILABLE FROM GUIDELINES GROUP.**

Analyte (exposure limits)	Standard Method	Sample Preparation Method	Sample Storage	Analysis	Ref
	determination; method not validated				
Sarin (GB) (HBESL _{ind} = 41 mg/kg)		20 mL liquid, 10 g metal, or 10 g soil collected		Extraction with chloroform; 40-150 µL extract into GC/FPD by thermal desorption; d. l. = 0.002-0.008 mg/kg	O'Neil 2002
Sarin (GB) (HBESL _{ind} = 41 mg/kg)		1 g soil extracted with 1 mL water (dichloromethane extraction also effective)		5 µL sample injected into LC/ESI/TOF/MS system; 10 mg/kg soil spikes could be detected; method also allowed detection of hydrolysis products	D'Agostino 2001
Soman (HBESL _{ind} = 8.2 mg/kg)	EPA Method 3541 for sample preparation; EPA Method 8270D for determination; method not validated	10 g sample processed by automated Soxhlet extraction	Store at 4°C for up to two weeks ^{EPA 1996}	GC/MS; d.l. ~ 0.7-3mg/kg	EPA 2004
Soman (HBESL _{ind} = 8.2 mg/kg)	EPA Method 3545A for sample preparation; EPA Method 8270D for determination; method not validated	10-30 g sample processed by pressurized fluid extraction	Store at 4°C for up to two weeks ^{EPA 1996}	GC/MS; d.l. ~ 0.7-3mg/kg	EPA 2004
Soman (GD) (HBESL _{ind} = 8.2 mg/kg)		20 mL liquid, 10 g metal, or 10 g soil collected		Extraction with chloroform; 40-150 µL extract into GC/FPD by thermal desorption; d. l. = 0.0004-0.001 mg/kg	O'Neil 2002
Soman (GD) (HBESL _{ind} = 8.2 mg/kg)		1 g soil extracted with 1 mL water (dichloromethane extraction also effective)		5 µL sample injected into LC/ESI/TOF/MS system; 10 mg/kg soil spikes could be detected; method also allowed detection of	D'Agostino 2001

Table 6. Characterization and clearance analysis methods for use with solid samples, including swipes. **NEED TO INCORPORATE SURFACE GUIDELINE LEVELS WHEN AVAILABLE FROM GUIDELINES GROUP.**

Analyte (exposure limits)	Standard Method	Sample Preparation Method	Sample Storage	Analysis	Ref
				hydrolysis products	
Sulfur Mustard (HBESL _{ind} = 14 mg/kg)	EPA Method 3541 for sample preparation; EPA Method 8270D for determination; method not validated	10 g sample processed by automated Soxhlet extraction	Store at 4°C for up to two weeks ^{EPA 1996}	GC/MS; d.l. ~ 0.7-3 mg/kg	EPA 2004
Sulfur Mustard (HBESL _{ind} = 14 mg/kg)	EPA Method 3545A for sample preparation; EPA Method 8270D for determination; method not validated	10-30 g sample processed by pressurized fluid extraction	Store at 4°C for up to two weeks ^{EPA 1996}	GC/MS; d.l. ~ 0.7-3 mg/kg	EPA 2004
Sulfur Mustard (HBESL _{ind} = 14 mg/kg)		Unspecified amount of solid concrete collected		Extraction with acetonitrile under elevated temperature (100°C) and pressure (1500 psig) and detection of various sulfur mustard degradation products at 2-13 mg/kg by GC/FPD	Tompkins 1997
Sulfur Mustard (HBESL _{ind} = 14 mg/kg)		1 g soil placed in vial		Water added and soil-water system sampled with polyacrylate or carbowax-divinylbenzene SPME fiber; d. l. ~0.24 mg/kg by GC/MS	Kimm 2002
Sulfur Mustard (HBESL _{ind} = 14 mg/kg)				Direct interrogation of sample by static secondary ion MS/MS; d.l. ~ 100 mg/kg	Gresham 2001
Tabun (HBESL _{ind} = 82 mg/kg)	EPA Method 3541 for sample preparation; EPA Method 8270D for determination; method not validated	10 g sample processed by automated Soxhlet extraction	Store at 4°C for up to two weeks ^{EPA 1996}	GC/MS; d.l. ~ 0.7-3 mg/kg	EPA 2004
Tabun (HBESL _{ind} = 82 mg/kg)	EPA Method 3545A for sample preparation; EPA	10-30 g sample processed by pressurized fluid	Store at 4°C for up to two weeks ^{EPA 1996}	GC/MS; d.l. ~ 0.7-3 mg/kg	EPA 2004

Table 6. Characterization and clearance analysis methods for use with solid samples, including swipes. **NEED TO INCORPORATE SURFACE GUIDELINE LEVELS WHEN AVAILABLE FROM GUIDELINES GROUP.**

Analyte (exposure limits)	Standard Method	Sample Preparation Method	Sample Storage	Analysis	Ref
	Method 8270D for determination; method not validated	extraction			
VX (HBESL _{ind} = 1.2 mg/kg)	EPA Method 3541 for sample preparation; EPA Method 8270D for determination; method not validated	10 g sample processed by automated Soxhlet extraction	Store at 4°C for up to two weeks ^{EPA 1996}	GC/MS; d.l. ~ 0.7-3 mg/kg	EPA 2004
VX (HBESL _{ind} = 1.2 mg/kg)	EPA Method 3545A for sample preparation; EPA Method 8270D for determination; method not validated	10-30 g sample processed by pressurized fluid extraction	Store at 4°C for up to two weeks ^{EPA 1996}	GC/MS; d.l. ~ 0.7-3 mg/kg	EPA 2004
VX (HBESL _{ind} = 1.2 mg/kg)				Direct interrogation of sample by static secondary ion MS/MS; d.l. ~ 1 mg/kg	Groenewold 2000
VX (HBESL _{ind} = 1.2 mg/kg)		5 g soil ultrasonically mixed with buffer solution and extracted with hexane/dichloromethane		GC/FPD; d.l. = 10 mg/kg soil	Montauban 2004

Abbreviations used in Table 6.

d.l. – detection limit; EPA – United States Environmental Protection Agency; GC/FPD – gas chromatography coupled with flame photometric detection; GC/MS – gas chromatography coupled with mass spectrometry; HBESL_{ind} – health-based environmental screening levels for industrial soil developed by the U.S. military and summarized in Raber 2004; LC/ESI/TOF/MS – Liquid chromatography coupled with electrospray ionization, time-of-flight mass spectrometry; MS/MS – tandem mass spectrometry; SPME – solid phase microextraction; VOC – volatile organic compound

Table 7. Characterization and clearance analysis methods for use with water samples. **NEED TO INCORPORATE SURFACE GUIDELINE LEVELS WHEN AVAILABLE FROM GUIDELINES GROUP.**

Analyte (exposure limits)	Standard Method	Sampling Preparation	Sample Storage	Analysis	Ref
Cyanogen chloride	EPA Method 5030 C for sample preparation; EPA Method 8260B for determination; not validated method	Collection of sample in vial	4°C for up to 14 days	Purge and trap coupled with GC/MS	EPA 2004
Hydrogen cyanide (EPA MCL for CN ⁻ = 0.2 mg/L)	EPA Method 335.4	Reflux-distillation of sample releases HCN into scrubber solution; CN ⁻ reacted with chloramine-T, then pyridine and barbituric acid to yield colored complex	Adjust water to pH \geq 12 with NaOH and store at 4°C for up to 14 days. Samples containing oxidizing agents, for example chlorine, must be treated with ascorbic acid	Colored complex is measured by spectrophotometry; d.l. = 0.005 mg/L	EPA 1993
Phosgene				Guidance in EPA documents suggests that phosgene will not be of concern in aqueous matrix	EPA 2004
Sarin	EPA Method 3520C for sample preparation; EPA Method 8270D for determination; method not validated	Typically, 1 L water extracted with immiscible solvent by continuous liquid-liquid extraction	Cool to 4°C; extract within 7 days; if sample contains residual chlorine, add sodium thiosulfate as preservative ^{EPA 1996}	GC/MS; d.l. ~ 10-1000 µg/L	EPA 2004
Sarin	EPA Method 3535A	Analytes isolated by solid	Cool to 4°C; extract	GC/MS; d.l. ~ 10-1000	EPA 2004

Table 7. Characterization and clearance analysis methods for use with water samples. **NEED TO INCORPORATE SURFACE GUIDELINE LEVELS WHEN AVAILABLE FROM GUIDELINES GROUP.**

Analyte (exposure limits)	Standard Method	Sampling Preparation	Sample Storage	Analysis	Ref
	for sample preparation; EPA Method 8270D for determination; method not validated	phase extraction from a typical sample size of 1 L	within 7 days; if sample contains residual chlorine, add sodium thiosulfate as preservative ^{EPA 1996}	µg/L	
Sarin		Direct collection of liquid		Decontamination solutions extracted with dichloromethane and analyzed by selected ion monitoring GC/MS; d.l. = 20 µg/L	Creasy 1999
Sarin		SDME		SDME coupled with GC/MS; d.l. = 75 µg/L	Palit 2005
Sarin				Direct injection of aqueous sample should provide d.l. ~ 10 mg/L by LC/ESI/MS	D'Agostino 1999
Soman	EPA Method 3520C for sample preparation; EPA Method 8270D for determination; method not validated	Typically, 1 L water extracted with immiscible solvent by continuous liquid-liquid extraction	Cool to 4°C; extract within 7 days; if sample contains residual chlorine, add sodium thiosulfate as preservative ^{EPA 1996}	GC/MS; d.l. ~ 10-1000 µg/L	EPA 2004
Soman	EPA Method 3535A for sample preparation; EPA Method 8270D for determination; method not validated	Analytes isolated by solid phase extraction from a typical sample size of 1 L	Cool to 4°C; extract within 7 days; if sample contains residual chlorine, add sodium thiosulfate as preservative ^{EPA 1996}	GC/MS; d.l. ~ 10-1000 µg/L	EPA 2004
Soman				Direct injection of	D'Agostino

Table 7. Characterization and clearance analysis methods for use with water samples. **NEED TO INCORPORATE SURFACE GUIDELINE LEVELS WHEN AVAILABLE FROM GUIDELINES GROUP.**

Analyte (exposure limits)	Standard Method	Sampling Preparation	Sample Storage	Analysis	Ref
				aqueous sample should provide d.l. ~ 10 mg/L by LC/ESI/MS	1999
Sulfur Mustard	EPA Method 3520C for sample preparation; EPA Method 8270D for determination; method not validated	Typically, 1 L water extracted with immiscible solvent by continuous liquid-liquid extraction	Cool to 4°C; extract within 7 days; if sample contains residual chlorine, add sodium thiosulfate as preservative ^{EPA 1996}	GC/MS; d.l. ~ 10-1000 µg/L	EPA 2004
Sulfur Mustard	EPA Method 3535A for sample preparation; EPA Method 8270D for determination; method not validated	Analytes isolated by solid phase extraction from a typical sample size of 1 L	Cool to 4°C; extract within 7 days; if sample contains residual chlorine, add sodium thiosulfate as preservative ^{EPA 1996}	GC/MS; d.l. ~ 10–1000 µg/L	EPA 2004
Sulfur Mustard		Direct collection of liquid		Decontamination solutions extracted with dichloromethane and analyzed by selected ion monitoring GC/MS; d.l. = 20 µg/L	Creasy 1999
Tabun	EPA Method 3520C for sample preparation; EPA Method 8270D for determination; method not validated	Typically, 1 L water extracted with immiscible solvent by continuous liquid-liquid extraction	Cool to 4°C; extract within 7 days; if sample contains residual chlorine, add sodium thiosulfate as preservative ^{EPA 1996}	GC/MS; d.l. ~ 10-1000 µg/L	EPA 2004
Tabun	EPA Method 3535A for sample preparation; EPA	Analytes isolated by solid phase extraction from a typical sample size of 1 L	Cool to 4°C; extract within 7 days; if sample contains	GC/MS; d.l. ~ 10–1000 µg/L	EPA 2004

Table 7. Characterization and clearance analysis methods for use with water samples. **NEED TO INCORPORATE SURFACE GUIDELINE LEVELS WHEN AVAILABLE FROM GUIDELINES GROUP.**

Analyte (exposure limits)	Standard Method	Sampling Preparation	Sample Storage	Analysis	Ref
	Method 8270D for determination; method not validated		residual chlorine, add sodium thiosulfate as preservative ^{EPA 1996}		
Tabun				Direct injection of aqueous sample should provide d.l. ~ 10 mg/L by LC/ESI/MS	D'Agostino 1999
VX	EPA Method 3520C for sample preparation; EPA Method 8270D for determination; method not validated	Typically, 1 L water extracted with immiscible solvent by continuous liquid-liquid extraction	Cool to 4°C; extract within 7 days; if sample contains residual chlorine, add sodium thiosulfate as preservative ^{EPA 1996}	GC/MS; d.l. ~ 10-1000 µg/L	EPA 2004
VX	EPA Method 3535A for sample preparation; EPA Method 8270D for determination; method not validated	Analytes isolated by solid phase extraction from a typical sample size of 1 L	Cool to 4°C; extract within 7 days; if sample contains residual chlorine, add sodium thiosulfate as preservative ^{EPA 1996}	GC/MS; d.l. ~ 10-1000 µg/L	EPA 2004
VX		Direct collection of liquid		Decontamination solutions extracted with dichloromethane and analyzed by selected ion monitoring GC/MS; d.l. = 20 µg/L; when interferences present, either reaction with silver fluoride or MS/MS needed to obtain d.l. = 20 µg/L	Creasy 1999

Table 7. Characterization and clearance analysis methods for use with water samples. **NEED TO INCORPORATE SURFACE GUIDELINE LEVELS WHEN AVAILABLE FROM GUIDELINES GROUP.**

Analyte (exposure limits)	Standard Method	Sampling Preparation	Sample Storage	Analysis	Ref
VX				Direct injection (10 µL) of 5 µg/L solution of VX (corresponding to 50 pg on-column) could be detected by LC/negative ESI/MS	Love 2004

Abbreviations used in Table 7.

d.l. – detection limit; EPA – United States Environmental Protection Agency; ESI/MS – electrospray ionization coupled with mass spectrometry; GC/FPD – gas chromatography coupled with flame photometric detection; GC/MS – gas chromatography coupled with mass spectrometry; LC – liquid chromatography; MCL = maximum contaminant level; SDME – single drop microextraction; SPME – solid phase microextraction; VOC – volatile organic compound

C.6. Monitoring of Decontamination Agents

In addition to monitoring a chemical agent to determine decontamination efficacy, it is also important to monitor the decontamination agent(s) themselves. This is important for two reasons - 1) to ensure that the decontamination agent was present at sufficient concentrations in various locations to inactivate the chemical agent and 2) to ensure that, after the decontamination process is complete, no decontamination agent remains at a concentration that would cause harm to human health.

Ideally, it should be required that the vendor providing decontamination services be responsible for identifying and monitoring parameters relating to the decontamination process. This would include monitoring environmental conditions such as ambient temperature, relative humidity, and airflow and decontamination agent concentration as the decontamination process proceeds. Concurrently with the previously mentioned monitoring, real-time or near real-time methods should be used by qualified individuals (possibly, but not necessarily, from the vendor providing decontamination), to monitor the chemical agent to verify decontamination progress. Such methods to analyze chemical agents have been previously discussed in Section C.4 of this appendix.

Suppose that modified vaporous hydrogen peroxide is to be used to provide agent decontamination. In this example, it would be important to monitor ambient temperature, relative humidity, airflow, hydrogen peroxide concentration, and ammonia concentration during the decontamination process. A multitude of sensors to measure temperature, humidity, and airflow are available and will not be discussed here. In order to monitor decontamination progress, it might be sufficient to use colorimetric strips, such as the Chemdi® VHP chemical indicator from Steris, to show that hydrogen peroxide vapor was present at sufficient concentrations at various locations to provide agent decontamination. If actual measurements of hydrogen peroxide and ammonia were needed, they could be monitored using an electrochemical sensor (such as those available from Dräger, whose ammonia sensor measures 300-1000 ppm concentrations and whose hydrogen peroxide sensor measures concentrations of 300-7000 ppm). Note that electrochemical sensors are prone to both positive and negative cross reactivities with other gases and that sensor sensitivity can change as much as 30% as exposure to the gas of interest continues. Near infrared spectroscopy might also be used to monitor real time concentrations of hydrogen peroxide and ammonia. However, the use of this technique would require validation to ensure that it did not respond to potential interferences known to be present at the location being decontaminated. IMS, such as the ProSentry-IMS by Particle Measuring Systems, could also be used

to monitor hydrogen peroxide and ammonia concentrations from part-per-billion to percent concentrations. In addition, a detector based on liquid-phase reaction of peroxides with *p*-hydroxyphenylacetic acid (and catalyzed by peroxidase) uses a fluorescence measurement to determine hydrogen peroxide is available (AL-2021 Hydrogen Peroxide in Air and Water Monitor, from Yankee Environmental Systems, Inc.). To ensure that complete decontamination of an area occurs, these sensors should be set in hard-to-reach corners and other areas of a room. Because all of the previously mentioned sensors can be susceptible to false positive detections caused by interferences, all of the sensors would need to be evaluated for their responses to commonly occurring environmental chemicals prior to being placed into service.

After the decontamination process is complete, clearance monitoring should be performed to show that no harmful concentrations of gaseous hydrogen peroxide or ammonia remain. In determining clearance criteria, health-based guidelines, for example the OSHA permissible exposure limit (PEL) for the decontamination agents, should be consulted ([does this agree with what the guidelines group would suggest?](#)). For example, the OSHA PEL of hydrogen peroxide is 1 ppm (1.4 mg/m³). Thus, the analytical method used to certify that hydrogen peroxide is not present at harmful levels should be capable of measuring hydrogen peroxide at or below this concentration. Dräger tubes can be used to sample air and measure concentrations of hydrogen peroxide in the air at 0.1-3 ppm. In addition, OSHA method ID 006, air sampling with an impinger containing titanium oxysulfate and spectroscopic determination of the formed titanium-hydrogen peroxide complex, can detect hydrogen peroxide at concentration as low as 0.06 mg H₂O₂/m³. OSHA method ID 126G, air sampling with an impinger containing titanium oxysulfate and detection of the formed titanium-hydrogen peroxide with differential pulse polarography, can measure hydrogen peroxide concentrations as low as 0.1 ppm. The OSHA PEL of ammonia is 50 ppm (although eye irritation can occur at a lower concentration of 20 ppm). Dräger tubes can be used to sample air and measure concentrations of ammonia in the air at concentrations as low as 0.25 ppm. OSHA Method ID-188 pumps air, containing ammonia, through carbon beads impregnated with sulfuric acid in a glass tube. The sample is desorbed from the beads with deionized water and ammonia is analyzed as the ammonium ion using an ion chromatograph; detection limits for ammonia are 0.6 ppm for a 24-hour air sample and 1.9 ppm for a 7.5 L air sample. Thus, for both hydrogen peroxide and ammonia, validated methods exist that are able to measure these contaminants at concentrations lower than those that would adversely affect human health.

In summary, during restoration, both the contaminant and the chemical(s) used for decontamination need to be monitored. The methods used will depend on the phase of the restoration, the questions being addressed, and the required detection limits. For example, real-time analytical methods will most likely be important for

measurements taken as decontamination is ongoing to show that the decontamination is effective. Lab-based methods that provide optimum (*ie.* the lowest, or best) detection limits will be important during the clearance process to show that no hazardous concentrations of chemicals remain.

C.7. Chemical Agent Sampling References

ASTM International (ASTM). 2004. Standard Guide for Selection of Sampling Equipment for Waste and Contaminated Media Data Collection Activities. ASTM D 6232.

Black, R. M; Muir, B. *J. Chromatogr. A.* **2003**, *1000*, 253-281.

Creasy, W. R.; Brickhouse, M. D.; Morrissey, K. M.; Stuff, J. R.; Cheicante, R. L. Jr.; Ruth, J.; Mays, J.; Williams, B. R.; O'Connor, R.; Durst, H. D.; *Environ. Sci. Technol.* **1999**, *33*, 2157-2162.

D'Agostino, P. A.; Provost, L. R.; Anacleto, J. F.; Brooks, P. W. *J. Chromatogr.* **1990**, *504*, 259-268.

D'Agostino, P. A.; Hancock, J. R.; Provost, L. R. *J. Chromatogr. A.* **1999**, *840*, 289-294.

D'Agostino, P. A.; Hancock, J. R.; Provost, L. R. *J. Chromatogr. A.* **2001**, *912*, 291-299.

EPA 1993. Method 335.4: Determination of Total Cyanide by Semi-automated Colorimetry, Rev 1.0, United States Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Office of Research and Development, Cincinnati, OH, 45268, August 1993.

EPA 1996. SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Rev. 3, Chapter 4, U.S. Environmental Protection Agency, 1996.

EPA 1997. Test Methods for Evaluating Solid Waste. SW-846 Third Edition, updated May 1997. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response Washington, DC. 20460.

EPA 2002. RCRA Waste Sampling Draft Technical Guidance Planning, Implementation, and Assessment. EPA530-D-02-002. August 2002. U.S. Environmental Protection Agency, access at:
<http://www.epa.gov/epaoswer/hazwaste/test/pdfs/rwsdtg.pdf>.

EPA 2004. Standardized Analytical Methods for Use During Homeland Security Events, Rev. 1.0, United States Environmental Protection Agency, Office of Research and Development, Washington DC 20460, EPA/600/R-04/126, September 2004, available at <http://www.epa.gov/ordnhsrc/pubs/reportSAM092904.pdf>.

Fowler, W. K. and Smith, J. E. Jr. *J. Chromatogr.* **1989**, 478, 51-61.

Gresham, G. L.; Groenewold, G. S.; Appelhans, A. D.; Olson, J. E.; Benson, M. T.; Jeffery, M. T.; Rowland, B.; Weibel, M. A. *Int. J. Mass Spectrom.* **2001**, 208, 135-145.

Groenewold, G. S.; Appelhans, A. D.; Gresham, G. L.; Olson, J. E.; Jeffery, M.; Weibel, M. *J. Amer. Soc. Mass Spectrom.* **2000**, 11, 69-77.

Kimm, G. L.; Hook, G. L.; Smith, P. A. *J. Chromatogr. A*, **2002**, 971, 185-191.

Love, A. H.; Vance, A. L.; Reynolds, J. G.; Davisson, M. L. *Chemosphere* **2004**, 57, 1257-1264.

Mesilaakso, M. Ed. 2005, Chemical Weapons Convention Chemicals Analysis: Sample collection, Preparation, and Analytical Methods, John Wiley and Sons Ltd.

Montauban, C.; Bégos, A.; Bellier, B. *Anal. Chem.* **2004**, 76, 2791-2797.

Naomi, M.; Kataoka, M.; Seto, Y. *Anal. Chem.* **2002**, 74, 4709-4715.

O'Neil, H. J.; Brubaker, K. L.; Schneider, J. F.; Sytsma, L. F.; Kimmell, T. A. *J. Chromatogr. A*, **2002**, 926, 183-195.

Palit, M.; Pardasani, D.; Gupta, A. K.; Dubey, D. K. *Anal. Chem.* **2005**, 77, 711-717.

Purdon, J. G.; Pagotto, J. G.; Miller, R. K. *J. Chromatogr. A*, **1989**, 475, 261-272.

Raber, E.; Carlsen, T.M.; Folks, K. J.; Kirvel, R. D.; Daniels, J. I.; Bogen, K. T. *Int. J. Environ. Health Res.* **2004**, 14, 31-41.

Rautio, M. 1993. Recommended Operating Procedures for Sampling and Analysis in the Verification of Chemical Disarmament. 1993 edition. The Ministry for Foreign Affairs of Finland, Helsinki 1993, ISBN 951-47-8164-3.

Schneider, J. F.; Boparail, A. S.; Reed, L. L. *J. Chromatogr. Sci.* **2001**, 39, 420-424.

Tompkins, B. A.; Sega, G. A.; MacNaughton, S. J. abstract from *Scientific Conference on Chemical and Biological Defense Research*, November 18-21, 1997.