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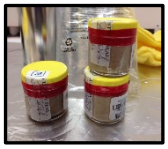
BUILDING A SCIENTIFIC FOUNDATION FOR SOUND ENVIRONMENTAL DECISIONS

Shipment, Preservation, and Analysis of Chemical Warfare Agents (CWAs) in Environmental Matrices



INTRODUCTION

Recent uses of chemical warfare agents (CWA) in the Middle East[1] and United Kingdom[2] have highlighted the need for methods to characterize the nature and extent of CWA contamination in the environment. CWA blister agents of concern include sulfur mustard (HD) Lewisite (L), while nerve agents of concern include cyclohexyl sarin (GF), sarin (GB), soman (GD), and O-ethyl-S-(2-diisopropylamino-ethyl)-methyl-phosphonothiolate (VX). The lethality of these agents requires verified and sensitive sampling and analysis methods.

The U.S. Environmental Protection Agency (EPA) is responsible for remediating civilian areas contaminated with CWAs. Historically there were a lack of available environmental CWA methods, making sample collection, preservation, and analysis challenging. Furthermore, the number of anticipated samples collected during remediation would have undoubtedly overwhelmed laboratory capacity and capability and delayed results needed to support decision-making during decontamination and clearance.

To address the challenge of a timely response and remediation effort, the EPA has developed the capability and capacity to handle these agents. Over twenty gas-chromatography mass spectrometry (GC-MS) analysis methods, liquid-chromatography mass spectrometry (LC-MS) analysis methods, and study reports were developed for use by EPA's national network of laboratories specifically dedicated to environmental samples, the Environmental Response Laboratory Network (ERLN) and the Water Laboratory Alliance (WLA). Study reports discuss the advantages and disadvantages of the available methods and other available resources for CWA analysis. All of the work, described herein, addresses the gap for improving laboratory capacity and capability to collect, preserve, handle, process, and analyze CWA samples in environmental matrices. Furthermore, these

U.S. EPA's Homeland Security Research Program (HSRP) develops products based on scientific research and technology evaluations. Our products and expertise are widely used in preventing, preparing for, and recovering from public health and environmental emergencies that arise from terrorist attacks, accidents, or natural disasters. Our research and products address biological, radiological, or chemical contaminants that could affect indoor areas, outdoor areas, or water infrastructure. HSRP provides these products, technical assistance, and expertise to support EPA's roles and responsibilities under the National Response Framework, statutory requirements, and Presidential Directives.

[1] Washington Post. https://www.washingtonpost.com/world/middle_east/global-watchdog-sarin-was-used-in-deadly-syria-attack/2017/04/19/be6cf350-2528-11e7-836b-e91b113bf060_story.html?noredirect=on&utm_term=.d98ee77f99cd (accessed September 2018))

[2] Novichok nerve agent use in Salisbury: UK government response, March to April 2018. https://www.gov.uk/government/news/novichok-nerve-agent-use-in-salisbury-uk-government-response (accessed September 2018)

methods and reports increase ERLN's capability and capacity to analyze environmental samples and ensure that analytical results generated by the various labs conducting analysis are comparable.

CHEMICAL WARFARE AGENT (CWA) ANALYTICAL METHOD DEVELOPMENT

HSRP initially developed CWA analytical methods for HD, GF, GB, and VX in various environmental matrix types (e.g., water, soil, surfaces). The CWA methods were multi-laboratory evaluated to verify their use for an environmental response. Method data are listed in Table 1. HSRP also established an ultra-dilute standards program for these CWAs. These standards are required for ERLN laboratories across the country to have the capability to store and analyze CWA contaminated samples. Ultra-dilute standards were evaluated, including the procedures for preservation, shipping, handling, and storage of the standards. These studies showed that ERLN laboratories can use the ultra-dilute standards up to six months, if preservation and storage requirements are followed.

These methods can be found within the EPA Homeland Security Research Program's (HSRP) Environmental Sampling and Analytical Methods Program (ESAM). ESAM is composed of documents and information supporting field and laboratory efforts for site characterization, remediation and release, including the Selected Analytical Methods for Environmental Remediation and Recovery (SAM) 2017 document. SAM provides the single best method for an analyte- environmental matrix pair, which for many of the CWAs is the HSRP-developed method. ESAM also contains Sample Collection Information Documents (SCIDs), which provide general sample collection, handling and shipping information for collection of samples analyzed using the specific methods listed in EPA's SAM document. These methods will improve data comparability and confidence, permit sharing of the sample load between laboratories, and simplify the task of outsourcing analytical support to the commercial laboratory sector, if required. In addition, use of these methods will help improve the follow-up activities of validating results, evaluating data, and creating and communicating risk-management decisions. Overall, ESAM facilitates a coordinated response to a chemical contamination incident.

ADDITIONAL CWA METHOD DEVELOPMENT AND STUDY REPORTS

HSRP developed additional CWA methods for Lewisite (L) and hazardous CWA degradation products [e.g., S-[2-(diisopropylamino)ethyl] hydrogen methylphosphonothioate (EA2192), 2-chlorovinylarsonous acid (CVAA), and (2-chlorovinyl)arsonic acid (CVAOA)] in various environmental matrices. Although these methods are not multi-laboratory verified, the method evaluation reports are available on EPA's Homeland Security webpage, ESAM, or in EPA's Science Inventory. These methods (and additional CWA degradation methods) are also available in SAM for the EPA and ERLN to use during characterization activities. Method data for these select agents and degradation products are listed in Table 1.

Table 1: Select CWA and CWA Degradation Methods*

Analyte	Method Detection Limit			Reporting Limit (mg/L)	Analytical Run Time (minutes)
	water (µg/L)	soil (µg/kg)	wipes (µg/wipe)		
GB	0.1	0.16	0.002	0.01	12.75
GD	0.08	0.12	0.003	0.005	12.75
GF	0.1	0.17	0.003	0.01	12.75
HD	0.08	0.09	0.003	0.005	12.75
VX	0.1	0.33	0.006	0.01	12.75

EA2192	0.013	-	-	0.000125	30
L	41	28	0.38	0.02	38
CVAA	41	28	0.38	0.02	38
CVAOA	41	28	0.38	0.02	38

* Information in table taken from the referenced methods. These methods were not developed for compliance monitoring and they should not be considered as having EPA approval for compliance monitoring or any other regulatory program.

LINKS TO CHEMICAL METHODS

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- ASTM. 2016. "Method D7599-16: Standard Test Method for Determination of Diethanolamine, Triethanolamine, *N*-Methyldiethanolamine and *N*-Ethyldiethanolamine in Water by Single Reaction Monitoring Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)." West Conshohocken, PA: ASTM International. http://www.astm.org/Standards/D7599.htm
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- ASTM. 2016. "Method E2838-11: Standard Test Method for Determination of Thiodiglycol on Wipes by Solvent Extraction Followed by Liquid Chromatography/Tandem Mass Spectrometry." West Conshohocken, PA: ASTM International. http://www.astm.org/Standards/E2838.htm
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- Sample Collection Information Document for Chemicals, Radiochemicals & Biotoxins (SCID) (EPA/600/R-17/389)
- Selected Analytical Methods for Environmental Remediation and Recovery (SAM)-2017 [(EPA/600/R-17/356) (accessed August 2018)]
- Shoemaker, J.A. 2009. "Method 538: Determination of Selected Organic Contaminants in Drinking Water by Direct Aqueous Injection-Liquid Chromatography/Tandem Mass Spectrometry (DAI-LC/MS/MS)," Revision 1.0. Cincinnati, OH: U.S. EPA. EPA/600/R-09/149U.S. EPA and CDC. 2011. "Surface Analysis Using Wipes for the Determination of Nitrogen Mustard Degradation Products by Liquid

Chromatography/Tandem Mass Spectrometry (LC/MS/MS)." Cincinnati, OH: U.S. EPA. EPA/600/R-11/143. http://www2.epa.gov/sites/production/files/2015-07/documents/epa-600-r-11-143.pdf

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CONTACT INFORMATION

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