Sample-preparation techniques for the analysis of chemical-warfare agents and related degradation products

Deme Pragney, U.V.R. Vijaya Saradhi

Chemical-warfare agents (CWAs) are toxic chemicals intended for use in mass destruction and terrorist attacks. Their presence in the environment is of great concern due to their rapid distribution and toxicity. The Organization for the Prohibition of Chemical Weapons conducts proficiency tests for the offsite analysis of samples contaminated with CWAs and their degradation or oxidation products.

In this article, we review recent trends in the development of sample-preparation techniques for efficient extraction of Chemical Weapons Convention-related chemicals from environmental and industrial samples. We discuss extraction methodologies (e.g., solvent extraction, solid-phase microextraction, solid-phase extraction, and gas-phase and headspace analysis) and their advances.

Keywords: Chemical-warfare agent (CWA); Chemical Weapons Convention (CWC); Degradation product; Extraction methodology; Gas-phase analysis; Headspace analysis; Oxidation product; Solid-phase microextraction (SPME); Solid-phase extraction (SPE); Solvent extraction

Deme Pragney,
U.V.R. Vijaya Saradhi*
National Centre
for Mass Spectrometry,
Indian Institute
of Chemical Technology,
Taranaka,
Hyderabad 500 007,
Andhra Pradesh, India

*Corresponding author.
Tel.: +91 40 27191347;
Fax: +91 40 27193156;
E-mail: saradhi@iict.res.in

1. Introduction

Chemical warfare agents (CWAs) are highly toxic chemicals that can be used as chemicals of mass destruction. They are lethal, not only to human beings but also to every living creature. CWAs were first used in large scale as chemicals for mass destruction during World War I.

A Chemical Weapons Convention (CWC) was formed in 1993 with the aims of prohibiting development, production, stockpiling, and use of CWA and their destruction. The CWC entered into force on 29 April 1997, and its signatories formed an organization called the Organization for the Prohibition of Chemical Weapons (OPCW), situated in The Hague, The Netherlands. The OPCW performs verification activities on a regular basis and can conduct challenge inspections to fulfill the requirements of the CWC. The OPCW can conduct both on-site and off-site analysis through its designated laboratories. It also conducts the required proficiency tests (PTs) to assess the competency of laboratories around the world to undertake the off-site analysis of samples obtained. The laboratories need to follow efficient analytical protocols for identifying the chemicals present in the given matrices [1].

CWC chemicals are grouped in three schedules:

(1) the first comprises the most toxic substances that are intended for use in mass destruction;
(2) the second comprises their precursors and degradation products; and,
(3) the third comprises starting materials and chemicals that can be used in assassinations.

Large numbers of chemical structures are possible when various permutations and combinations of the alkyl groups described in the schedules are used. The samples, sent for analysis during the PTs conducted by the OPCW for off-site analysis for identification of these scheduled chemicals, are spiked with any chemical from these three schedules. Moreover, the chemicals may undergo various transformations (e.g., degradation, oxidation, and

0165-9936/$ - see front matter © 2012 Elsevier Ltd. All rights reserved. doi:http://dx.doi.org/10.1016/j.trac.2012.03.007

Table 1. List of analytical methods used for different classes of Chemical Weapons Convention (CWC) chemicals

Compounds	Matrix	Extraction procedure	Detection method	Ref.
Organophosphorous chemicals				
Sarin, Soman, Tabun, Vx and related toxic chemicals	Organic liquid	Extraction with acetonitrile	GC-MS	[13–15]
	Painted wall board	Dichloromethane: acetone in 1:1		[16]
	Soil	Dichloromethane and hexane mixture	GC-FPD	[17]
	Water	Methylene chloride and acetone, 1:1	GC-FPD	[18]
	Soil	Water by ultrasonic extraction	LC-ESI-MS	[24]
	Water	CH_2Cl_2/CCl_4 (3:1 v/v), SDME	GC-MS	[28]
	Water	Hollow fiber-protected liquid-phase microextraction	GC-MS	[33]
	Hexane	Phenol-based polymer BSP3 and BSP3 (b) SPME	GC-FID	[45]
	Water	SPME-PDMS and PDMS-DVB	GC-MS	[46]
	Soil	SPME-polydimethylsiloxane-coated fiber	GC-MS	[48]
	Office media (floor, paper)	SPME, PDMS	LC-ESI/DESI-MS/MS	[55,56]
	Water	SPE, multiwalled carbon nanotubes	GC-MS	[60]
	Water	SPE, Oasis HLB	GC-MS	[62]
	Water	Online SPE, strong cation exchange	HPLC-UV-NMR	[64]
	Soil	Oasis HLB and HR-P resins	LC–MS	[79]
	Soil	Molecularly imprinted and non-imprinted polymer	LC–MS	[80]
	Air	Depot area air-monitoring system (DAAMS)	LC-MS/MS	[88]
	Air	Adsorbing with ethyl acetate and hexane	GC-FPD/TSD	[89]
	Painted plates	Supercritical fluid extraction (SFE)	GC-MS	[97]
Organophosphonates and phosphoramidates	Water	SPE, multiwalled carbon nanotubes	GC-MS	[60]
	Complex organic matrix	SPE, ODS C18 cartridge	GC-MS	[82]
	Soil	Supercritical fluid and pressurized liquid extraction	GC-FPD-P/FID	[96]
Phosphonic acids and related degradation products	Soil	Dichloromethane and hexane mixture	GC-FPD	[17]
	Water	DCM, ether LLE	GC-MS	[19]
	Soil	Water	LC-ESI MS	[24]
	Water	Ion-pair liquid–liquid–liquid microextraction	CE-CCD	[29]
	Water	Hollow fiber-liquid-phase microextraction and SPME	GC-MS	[38]
	Water	SPME-PDMS and PDMS-DVB	GC-MS	[46]
	Beverages	Strata-X solid-phase extraction cartridges	LC-MS/MS	[61]
	Soil	SPE, cation-exchange resin	GC-MS	[65]
	Water	SPE, Oasis mixed-mode anion exchange	LC–UV–NMR	[66,67]
	Soil	Pressure-assisted solvent extraction with water	CE- ion trap MS	[75]
	Water	Ion-pair (IP) solid-phase extraction	GC-MS	[77,78]
	Water	Zirconia hollow fiber	LC-MS and LC-SCD	[83,84]
	Water	Electro membrane isolation (PP-EMI) with 1-octanol	CE-CCD	[95]
	Water	Acetonitrile extract and direct derivatization	GC-EI/CI-MS	[98]
	–	Injection port fluorination with trifluoroacetic anhydride	GC-MS	[99]
	Soil	Water, ultrasonic extraction	LC-ESI MS	[20–22]
Organosulfur and nitrogen chemicals	Soil	Acetonitrile by OMDEX method	GC-MS	[23]
	Water	CH_2Cl_2/CCl_4 (3:1 v/v), SDME	GC-MS	[28]
	Water	Hollow fiber-protected liquid-phase microextraction	GC-MS	[33]
	Soil	HS-SPME, polyacrylate and Carbowax-DVB coatings	GC-MS	[47,49]
	Water	SBSE	GC-FPD	[58]
	Water	SPE, multiwalled carbon nanotubes	GC-MS	[60]
	Water	SPE, Oasis HLB	GC-MS	[62]
	Water and human plasma	Silica- and polymer-based SCX SPE	GC-MS	[63]
	Water	Online SPE, Strong cation exchange	HPLC-UV-NMR	[64]
	Air and DAAMS	C8 solid-phase extraction	TD-GC-NPD and GC-MS	[90]
	Soil	Water saturated with NaCl, Head space-trap	GC-MS	[91]
	Water	headspace-trap	GC-MS	[92]
	Air	Richter or Zaitsev vessel absorber and 0.5% of Apiezon L on Silochrom S-120 adsorbent	GC-ECD and FID	[93]

(*continued on next page*)