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United States
Environmental Protection
Agency

Testing and Quality Assurance Plan for the Evaluation of Wipe Sampling Methods for Collecting Chemical Warfare Agents (CWAs), CWA Degradation Products, and Toxic Industrial Chemicals from Various Surfaces

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Prepared for

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Notice

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Abstract

Wipe sampling is an important technique for the estimation of contaminant deposition on surfaces. Numerous wipe sampling methods exist, and each method has its own specification for the type of wipe, wetting solvent, extraction procedure, and determinative step to be used, depending upon the contaminant of concern. Wipe sampling methods for the purposes of analytical determination of surface contamination largely do not exist for compounds of interest to the homeland security community. The goal of the project is to provide a wipe sampling method or methods and associated method performance data for collecting selected chemical warfare agents (CWAs), CWA degradation products, and toxic industrial chemicals from five types of surfaces (laminate, galvanized metal, bare wood, industrial carpet, and painted concrete). The objective of this testing and quality assurance plan is to present procedures for testing, which will include documenting the performance of the methods at or below residential risk-based cleanup goals. Testing will be conducted under the U.S. Environmental Protection Agency's National Homeland Security Research Center's Technology Testing and Evaluation Program. Note that an addendum has been added to this document as an appendix which addresses modifications to this plan which were made after the start of testing.

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Abbreviations, Acronyms, and Symbols

%D	percent difference
µL	microliter
ASE	accelerated solvent extraction
ASTM	American Society for Testing and Materials
CAC	Columbus Analytical Chemistry
CCV	Continuing Calibration and Verification
CHP	Chemical Hygiene Plan
cm	centimeter
cm^2	square centimeter
CWA	chemical warfare agent
DCM	dichloromethane
EPA	U.S. Environmental Protection Agency
ESI	electrospray ionization
GC	gas chromatography
GD	soman
HD	distilled mustard
HN-3	nitrogen mustard 3
HPLC	high-performance liquid chromatography
HRMS	high resolution mass spectrometry
IPA	isopropanol or isopropyl alcohol
LC	liquid chromatography
LRB	laboratory record book
LRMS	low resolution mass spectrometry
mL	milliliter
mm	millimeter
MPA	methyl phosphonic acid
MS	mass spectrometry
MS/MS	tandem mass spectrometry
NERL	National Exposure Research Laboratory
NHSRC	National Homeland Security Research Center
OP	organophosphate pesticide
PEG	polyethylene glycol
PFK	perfluorokerosene
PFTBA	perfluorotributylamine
PMPA	pinacolylmethylphosphonic acid
PSP	Physical Security Plan
QA	quality assurance
QC	quality control
QMP	Quality Management Plan
RDTE	Research, Development, Testing and Evaluation
SIM	selected ion monitoring
SOP	standard operating procedure

TDG	thiodiglycol
TEPP	tetraethyl pyrophosphate
TL	team leader
TOL	task order leader
TOPO	Task Order Project Officer
TQAP	testing and quality assurance plan
TTEP	Technology Testing and Evaluation Program
VX	O-ethyl-S-[2(diisopropylamino)ethyl] methylphosphonothiolate

Acknowledgements

This testing and quality assurance plan (TQAP) was prepared by Battelle for the U.S. Environmental Protection Agency (EPA) Technology Testing and Evaluation Program (TTEP) under the direction and coordination of Stephen Billets of the EPA's National Exposure Research Laboratory (NERL), Environmental Sciences Division, in Las Vegas, Nevada. Funding support for this project was provided by EPA's National Homeland Security Research Center (NHSRC). EPA NERL recognizes Oba Vincent, Rob Rothman, and Eric Koglin from EPA NHSRC for their contributions. EPA NERL thanks the following peer reviewers for their review of this TQAP: Doug Anders and Sheri Bettis of the FBI, Lisa Detter-Hoskin of Georgia Tech Research Institute, Ted Haigh and Lawrence Zintek of EPA/Region 5, Carolyn Koester of Lawrence Livermore National Laboratory, Lisa Jo Melnyk and Jeff Morgan of EPA/ORD/NERL, Jack Pretty CEMB/DART/NIOSH, and Terry Smith of EPA/OSWER.

A
Project Management

A1. Background

Wipe sampling is one of the primary techniques for assessing surface contamination in a variety of applications including monitoring in environmental, industrial hygiene, remedial, security, and compliance scenarios (*1*). When implemented following a validated method, the technique is a quick and easy means of assessing the level or degree of contamination that may reside on the surface.

Procedures for the collection of contaminants from surfaces have several components in common, including the wipe sampling media, the wetting solvent, and the collection technique (*1*). However, wipe sampling procedures can vary widely, depending on the contaminant(s) of interest and the surface to be sampled. Reliability of the sample results begins with accurate and reproducible collection of a sample for analysis. Thus, the wipe sampling procedures used for a particular analyte on a given surface, including the proper combination of the wipe sampling components described above, are an integral aspect of whether or not the results generated will be representative of the contamination (*1*).

A recent literature study completed by U.S. Environmental Protection Agency (EPA) found that wipe sampling is widely used in industrial hygiene, drug enforcement, exposure risk assessment, and other related applications. However, very little performance data for any of these applications was located and no information on the compounds of interest to the homeland security community was found (*1*).

Four of the 15 Department of Homeland Security Planning Scenarios address various forms of a chemical attack on and in buildings, structures, and outdoor spaces (*2*). Those responsible for the cleanup of contaminated structures must understand the nature and extent of the contamination on various surfaces. However, collecting a sample of a contaminant of interest from a surface that is representative of the concentration present at the location has proven difficult and there is no one agreed upon or recognized method for sample collection. To address this deficiency, EPA's National Homeland Security Research Center (NHSRC) intends to provide a wipe sampling method or methods that can be used to collect selected chemical warfare agents (CWAs), their degradation products, and other toxic industrial chemicals (TICs) from a variety of non-porous and porous surfaces. In developing a wipe sampling method or methods, two different scenarios are considered:

Emergency Response Scenario: Wipe sampling would be used immediately following an incident. Sampling will need to occur quickly and it would be used to collect the parent agent or agents because there would have been little time for degradation to occur. Also, the concentration of the contaminants would be at their highest.

Cleanup or Clearance Scenario: Wipe sampling will be more thorough and less hurried. Degradation products may be more abundant than the parent compounds and at concentrations far lower than were originally present immediately following an incident. Therefore, the sampling method must be compatible with more sensitive and selective analytical methods.

The emergency response and consequence management communities need validated and reliable wipe sampling methods to address the above scenarios, and this project intends to address this need with emphasis on the Cleanup Scenario. Exposure to CWAs and TICs can occur through routes of inhalation of the vapor and/or aerosol, dermal absorption of the aerosol, and ingestion of contaminated food and non-food items. After a release incident, individuals may also become exposed by living near accident sites, touching contaminated surfaces, or consuming contaminated water or food. It is necessary to establish health-based benchmarks for the contaminants of health concern in support of the cleanup efforts in case of a release of CWAs or TICs. Provisional risk-based cleanup goals for selected CWAs and TICs have been established by the Threat and Consequence Assessment Division of EPA NHSRC based on the document established by the Contaminants of Potential Concern (COPC) Committee of the World Trade Center Indoor Air Task Force Working Group and an on-going effort to update the EPA Risk Assessment Guidance for Superfund (RAGS), Part E, Dermal Guidance (*3*,*4)*. Since the objective in the Cleanup Scenario is ultra-low sensitivities to identify human exposure issues, pre-cleaned wipes, which offer a lower chance of analytical interferences, and sensitive analytical techniques (e.g., selected ion monitoring high resolution mass spectrometry and tandem mass spectrometry) will be utilized.

This project represents the second phase of a four-phase effort planned by EPA NHSRC. The first phase was the literature review. This phase will focus on determining a method addressing the Cleanup Scenario with a subset of the target analyte list. The third phase will involve a single-laboratory validation of the method determined by this project with the full suite of target analytes. The fourth phase will be a round-robin study of the validated method.

A2. Testing and Quality Assurance Plan Description

The objective of this testing and quality assurance plan (TQAP) is to evaluate a wipe sampling method or methods that can be used to collect selected CWAs, their degradation products, and toxic industrial chemicals (specifically organophosphorous pesticides or OPs) from a variety of non-porous and porous surfaces. This study, which will be conducted under NHSRC's Technology Testing and Evaluation Program (TTEP) in compliance with the program's quality management plan (QMP) *(5)*, will provide recovery and reproducibility data that can be used to assess the efficiency of the sampling method for selected compounds. This TQAP describes the procedures that will be used to conduct the wipe sampling method evaluation. The primary sections of this TQAP include:

- Section A, Project Management, describes project history and objectives, roles and responsibilities of the participants, and documents project planning.
- Section B, Measurement and Data Acquisition, covers the experimental aspects of the project, including design, implementation, and quality control.
- Section C, Data Management, details the data handling, evaluation, archival, and reporting procedures.

- Section D, Health and Safety, highlights health and safety aspects of the study, including handling of chemical agents.
- Section E, References, includes citations for the documents referenced in this TQAP.

A3. Schedule

Table 1 describes the schedule for this project. The schedule details the major milestones for the experimental work, which is anticipated to take four months to complete. A draft wipe sampling method will be provided to EPA by June 23, 2008. The peer-reviewed report, which will include the final method, will be submitted to EPA by September 30, 2008.

Table 1. Project Schedule

Activity	Target Completion Date
Perform Phase I Experiments	March 14, 2008
Perform Phase II Experiments	May 30, 2008
Compile and evaluate data	June 16, 2008
Provide draft method to EPA	June 23, 2008
First draft report to EPA	July 11, 2008
Revised draft report submitted to EPA for peer review	August 14, 2008
Final report submitted to EPA	September 30, 2008

A4. Roles and Responsibilities

The responsibilities of the key participants in this project are described in this section. Figure 1 is an organization chart showing the relationship between the key participants.

A4.1. Battelle

Ms. Amy Dindal is the Battelle's Task Order Leader (TOL) for this project. In this role, Ms. Dindal will have overall responsibility for ensuring that the technical, schedule, and cost goals established for the project are met. Specifically, Ms. Dindal will:

- Contribute to preparation of the TQAP, wipe sample collection method(s), and project report.
- Revise the draft TQAP, wipe sample collection method(s), and project report in response to reviewers' comments.
- Coordinate distribution of the final TQAP, wipe sample collection method(s), and project report.
- Manage staff to ensure the budget is not exceeded and schedule is met.
- Ensure that necessary Battelle resources, including staff and facilities, are committed to the verification test.
- Assist Battelle team leaders and technical staff as needed in performing the project in accordance with this TQAP.
- Serve as the primary point of contact for EPA.

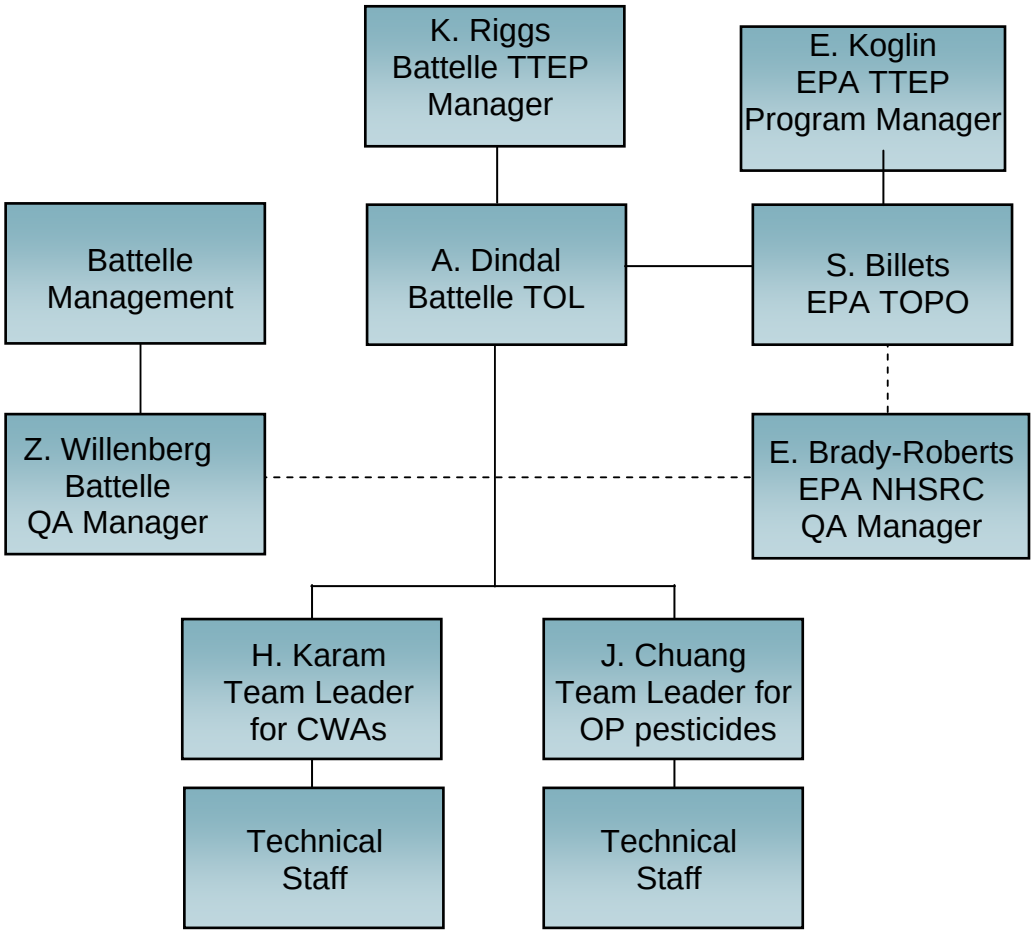

Figure 1. Organizational Chart of Key Participants
(dotted line indicates indirect reporting)

Dr. Hani Karam is Battelle's team leader (TL) for the CWA analyses with the responsibility for coordinating and overseeing sample analyses, data interpretation, and data reporting for CWAs and their degradation products. As such, Dr. Karam will:

- Contribute to the TQAP, wipe sample collection method(s), and project report, with primary responsibility for the sections related to CWA and CWA degradation product analyses.
- Oversee the execution of the Battelle technical staff performing the CWA and CWA degradation product analyses.
- Compile and evaluate data generated from the CWA testing.
- Maintain communication with Battelle's TOL.

Ms. Jane Chuang is Battelle's TL with the responsibility for coordinating and overseeing sample analyses, data interpretation, and data reporting for OPs. As such, Ms. Chuang will:

- Contribute to the TQAP, wipe sample collection method(s), and project report, with primary responsibility for the sections related to OP pesticide analyses.

- Oversee the execution of the Battelle technical staff performing the OP pesticide analyses.
- Compile and evaluate data generated from the OP pesticide testing.
- Maintain communication with Battelle's TOL.

Mr. Zachary Willenberg is Battelle's QA Manager for this project. Mr. Willenberg will:

- Review and approve the draft and final TQAP.
- Conduct a technical systems audit at least once during the technology evaluation.
- Audit at least 10% of the evaluation data.
- Notify Battelle's TTEP Manager to issue a stop work order if internal audits indicate that data quality is being compromised.
- Review and approve the draft and final wipe sample collection method(s).
- Review and approve the draft and final project report.

Ms. Karen Riggs is Battelle's TTEP Manager. As such, Ms. Riggs will:

- Review and approve the draft and final TQAP.
- Ensure that necessary Battelle resources, including staff and facilities, are committed to the project.
- Provide the TOPO with monthly technical and financial progress reports.
- Monitor adherence to budgets and schedules in this work.
- Review and approve the draft and final wipe sample collection method(s).
- Review and approve the draft and final project report.
- Issue a stop-work-order if internal audits indicate that data quality is being compromised.

A4.2. EPA

Dr. Stephen Billets is EPA's Task Order Project Officer (TOPO) for this project. Dr. Billets will:

- Review and approve the draft and final TQAP, wipe sample collection method(s), and project report.
- Provide technical guidance as appropriate to address the needs of EPA.
- Make technical decisions regarding the direction of the work such as implementing options.
- Oversee the EPA review process, including securing reviewers, for the TQAP and project report.

Ms. Eletha Brady-Roberts is EPA NHSRC QA Manager. Ms. Brady-Roberts will:

- Review and approve the draft and final TQAP.
- Review the draft and final wipe sample collection method(s).
- Review the draft and final project report.
- Notify the EPA TOPO to contact the Battelle TTEP Manager to issue a stop work order if an external audit indicates that data quality is being compromised.

Mr. Eric Koglin is the EPA TTEP Program Manager who directs Battelle's activities on the contract, "Testing and Investigation of Homeland Security-Related Technologies for the Measurement, Sampling, Removal, and Decontamination of Chemical and Biological Agents" under which TTEP has been established.

B
Measurement and Data Acquisition

The section covers the experimental aspects of the project including experimental design, implementation, and quality control.

B1. Experimental Plan

A recent literature review study (*1*) indicated that virtually no wipe sampling method performance information is available for collecting CWAs and CWA degradation products from various types of surfaces. The American Society for Testing and Materials (ASTM) has a wipe sampling method for organic compounds (e.g., pesticides, Aroclors) from non-porous surfaces *(6)* and a recent study discussed wipe sampling method for pesticides from porous and non-porous surfaces *(7)*. However, there is no precision and accuracy data for CWAs and CWA degradation products reported in the literature to document the performance of the wipe sampling method(s). The main objective of this project is to prepare a robust and reproducible standard method for the collection of target analytes including CWAs, CWA degradation products, and selected OPs from five types of surfaces (i.e., laminate, galvanized metal, bare wood, industrial carpet, and painted concrete) at or below residential risk-based cleanup goals. The general approach for evaluating the wipe sampling method(s) to be established consists of:

- Applying a known amount of target compound(s) onto test coupons made from different surface materials,
- Wiping test coupons with a pre-cleaned wiping material wetted with solvent to remove and collect the spiked target compounds,
- Determining the recovery of the spiked target compounds using established analytical method(s), and
- Incorporating quality assurance (QA)/quality control (QC) measures to monitor method performance in each phase of the process.

A two-phase experimental design (Figure 2) will be used to carry out experiments to accomplish this objective. Phase I will establish a robust, reproducible, and reliable wipe sampling method for the target analytes on a non-porous surface (i.e., laminate) at a single (mid-range or 5x) concentration level. Phase II will evaluate the performance of the method established in Phase I on all five types of surfaces at three concentration levels and modify the method if necessary.

The key hypotheses to be tested in Phase I are:

1. Comparable results are obtained between a streamlined multi-analyte spiking method and a straight forward single-analyte spiking method
2. Quantitative and reproducible recoveries of the target analytes from spiked non-porous test coupons (i.e., laminate) are obtained
3. Consistent results are obtained between horizontal and vertical wiping methods.

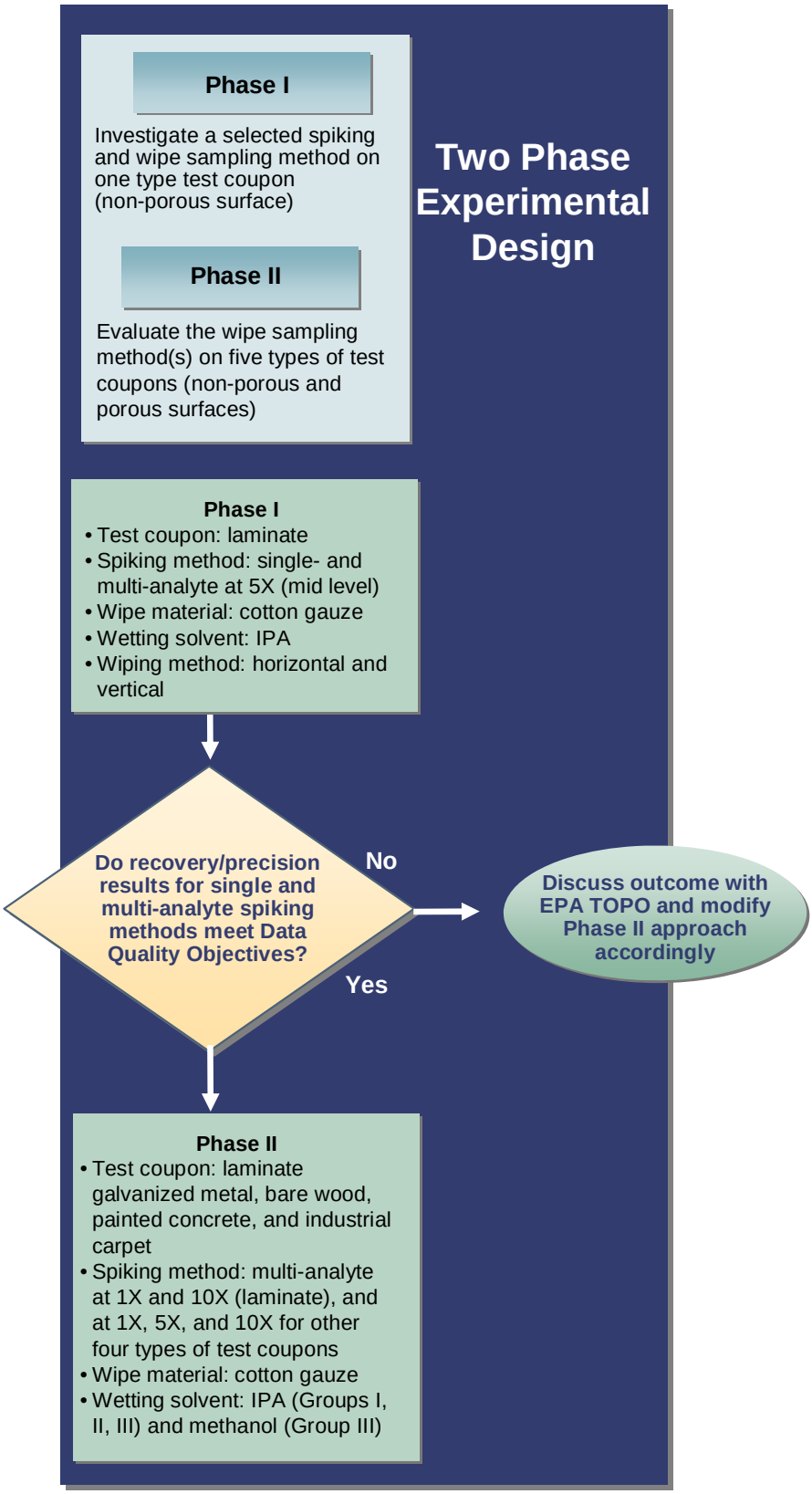

Figure 2. Phase I and Phase II Experiments

Note that the term "horizontal wiping method" used in the TQAP means to place the test coupon flat (e.g., representing floor surfaces) in the hood for wiping, and the term "vertical wiping method" means to place the test coupon vertically with a back support (e.g., representing wall surfaces) for wiping.

According to the literature review results and the ASTM method (*1,6*), cotton gauze is a commonly used wiping material and isopropanol (IPA) is a commonly used wetting solvent for similar compounds, so when considering the nature of the target analytes, this combination was chosen as a starting point for the Phase I study.

The recovery data obtained from Phase I will be evaluated in terms of data quality objective goals. These goals are:

- The percent difference (%D) values of the mean recovery data of field spiked coupon samples derived from single- versus multi-analyte spiking as well as horizontal versus vertical methods are within ±10%
- The average recovery data of triplicate field spiked coupon samples range from 70 to 110% and % relative standard deviation (% RSD) values of triplicate field spiked samples are within ±20%.

Battelle will discuss the results of Phase I with the EPA TOPO and determine whether it is feasible to move forward to Phase II experiments as outlined in Figure 2. If the results from Phase I experiments do not meet all the criteria as stated above, Battelle will consult with the EPA TOPO on revising the approach for the Phase II full-scale study accordingly.

The Phase II experiments outlined in Figure 2 are based on the assumption that satisfactory results are achieved for the Phase I hypotheses. Thus, multi-analyte spiking and cotton gauze wetted with IPA are planned for the Phase II full-scale study. In addition, Battelle will also examine a second wetting solvent (e.g., methanol) for the more polar target analytes in Group III (as defined below) to determine if improved performance can be achieved with methanol for these target analytes.

Technical challenges are expected in Phase II experiments when different types of surfaces are tested with the wipe sampling method(s). For example, the galvanized-metal surfaces may react with selected CWAs such as VX and cause reduced recoveries of the target analyte from the surface. Painted concrete surface could present potential matrix interference for the analytical methods. Relatively lower recoveries for the spiked field samples are expected for porous surfaces (i.e., bare wood and industrial carpet) as compared to non-porous surfaces because the porous surface materials tend to absorb the spiked compounds and lower the sample wiping efficiency. Battelle's experimental design takes into consideration these technical challenges. The CWA degradation products, 1,4-dithiane and 1,4-thioxane, will be monitored for CWA-spiked test coupons in an attempt to determine if degradation of HD occurs on the spiked surfaces. Six types of QC samples (described in Section B2.7) are included to document precision and accuracy of the analytical methods employed and potential sample matrix effect. Detailed discussion of the experimental design is described below.

B1.1. Target Analytes and Analyte Groups

A list of compounds of interest to the EPA with the associated Provisional Risk-based Surface Cleanup Goals *(3,4)* is presented in Table 2. The wipe sampling method(s) to be evaluated will

be developed for test coupons challenged with target analytes at or below the Provisional Risk-based Surface Cleanup Goals to ensure the adequacy of the wipe sampling method(s) to address the detection of such low levels of contaminants, for public health safety reasons. A subset of the compounds listed in Table 2 will be studied in this project while all the Table 2 compounds will be challenged in a future EPA NHSRC single laboratory validation study using the optimized wipe sampling method(s) established here. As shown in Table 3, a total of ten target analytes, including five selected by EPA marked with an asterisk and five selected by Battelle marked with two asterisks, will be studied in this project.

Table 3 summarizes the estimated instrument detection limits in terms of micrograms per sample (µg/sample) and micrograms per square centimeter (µg/cm^2) for these 10 target analytes, the analytical methods to be used for their analysis, the proposed spiking levels, and Battelle's rationale for the inclusion of a second target compound in each class. Chemical structures for the 10 compounds of interest are presented in the Appendix A.

According to the chemical/physical properties and established analytical methods, the 10 target compounds will be split into three groups. Group I will consist of the target CWAs, namely HD, HN-3, GD, and VX. Group II will contain CWA degradation product (1,4-dithiane) and OP pesticides (dichlorvos and tetraethylpyrophosphate (TEPP). The more polar CWA hydrolysis products thiodiglycol (TDG), pinacolylmethylphosphonic acid (PMPA), and methylphosphonic acid (MPA) will be in Group III.

Based on Battelle's experience with these target compounds from other previous studies (*8*), the interactions of the target compounds in each group should be negligible. As outlined in Figure 2 and described in section B1, multi-analyte spiking method is proposed for the Phase II full-scale study. However, as a quality assurance measure, spike recovery experiments will be performed using both the single- and multi-analyte spiking methods on laminate surface at 5X spiking levels in triplicate in Phase I experiments. One target analyte from each of the three groups will be used (GD from Group I, dichlorvos from Group II, and PMPA from Group III) for the single-analyte spiking method. Each of the three analyte groups containing multi-analytes as discussed above will be used in the multi-analyte spiking method.

B1.2. Concentration Levels for Test Coupons

Three concentration levels (i.e., 1x, 5x, and 10x) will be used to prepare test coupons (Table 3). The lowest concentration level (1x) for all the target analytes to be spiked onto the test coupons is set at or below residential Risk-Based Surface Cleanup Goals. As shown in Table 2, residential risk-based surface cleanup goals are available for six target analytes (HD, GD, VX, 1,4-dithiane, dichlorvos, MPA) but not for HN-3, TDG, PMPA, and TEPP. An assumption is made that compounds in the same compound class would have similar risk-based surface cleanup goal. Thus, the Risk-Based Surface Cleanup Goals assigned for HN-3 and TEPP are the same as HD and dichlorvos, respectively (Table 3). Target analytes with fairly high Risk-Based Surface Cleanup Goals (1,4-dithiane and MPA) or no known Risk-Based Surface Cleanup Goals (TDG and PMPA) will be spiked at three concentration levels of multiples of the established instrument detection limits for these analytes (Table 3). Table 4 compares the proposed 1x concentration spiking level of target analytes to the Risk-Based Surface Cleanup Goal and summarizes the concentrations of target analytes in the spiking solutions required to accomplish the 1x spiking level in both single- and multi-analyte spiking methods

Table 2. Provisional Risk-Based Surface Cleanup Goals for Target Compounds

Compound Class	Compound [a]	CAS	Risk-based Surface Cleanup Goals (µg/cm^2)	
			Occupational [b]	Residential [c]
CWA – Blister Agents	*Distilled Mustard (HD)	505-60-2	0.00022	.000081
	Mustard (T)	172672-28-5	--[d]	--[d]
	Mustard, nitrogen (HN-1)	538-07-08	--[e]	--[e]
	Mustard, nitrogen (HN-2)	51-75-2	--[e]	--[e]
	Mustard, nitrogen (HN-3)	555-77-1	--[e]	--[e]
CWA – Blister Agent Degradation Products	*1,4-Dithiane	505-29-3	6.0	2.1
	1,4-Thioxane	15980-15-1	--[d]	--[d]
	Thiodiglycol	111-48-8	--[d]	--[d]
Nitrogen Mustards Degradation Products	N-Ethyldiethanolamine	139-87-7	--[f]	--[f]
	N-Methyldiethanolamine	105-59-9	--[f]	--[f]
	Triethanolamine	102-71-6	--[f]	--[f]
CWA – Nerve Agents	Sarin (GB)	107-44-8	0.012	0.0043
	Soman (GD1 and GD2)	96-64-0	0.0024	0.00086
	Tabun (GA)	77-81-6	0.024	0.0086
	*VX	501782-69-9	0.00036	0.00013
	Cyclohexyl Sarin (GF)	329-99-7	--[d]	--[d]
CWA – Nerve Agent Precursors and Degradation Products	Dimethylphosphite	868-85-9	--[d]	--[d]
	Diisopropyl methyl phosphonate	1445-75-6	48.0	17.0
	Dimethylphosphoramidic acid	33876-51-6	--[d]	--[d]
	EA 2192 (S-2-diisopropylaminoethyl methylphosphonothionic acid)	73207-98-4	--[d]	--[d]
	Ethylmethyl phosphonic acid	1832-53-7	--[d]	--[d]
	Isopropyl methylphosphonic acid	1832-54-8	60.0	21.0
	*Methylphosphonic acid	993-13-5	15.0	5.2
	Cyclohexylmethylphosphonic acid	1932-60-1	--[d]	--[d]
	Pinacolylmethylphosphonic acid	616-52-4	--[d]	--[d]
OP Pesticides	*Dichlorvos	62-73-7	0.0058	0.0022
	Dicrotophos	141-66-2	0.06	0.021
	Fenamiphos	22224-92-6	0.15	0.054
	Methyl parathion	298-00-0	0.15	0.054
	Mevinphos	7786-34-7	--[d]	--[d]
	Phorate	298-02-2	0.12	0.043
	Tetraethylpyrophosphate	107-49-3	--[d]	--[d]
	Crimidine	535-89-7	--[d]	--[d]

[a] * denotes compounds designated by EPA to be included in this project

[b] Occupational – Exposures for non-porous surfaces. Exposure assumptions are for adults for 25 years, 8 hours/day, 250 days/year; exposure pathways include dermal and oral associated with hand-to-mouth activity. Inhalation exposures are not included in this evaluation. Values are provisional only.

[c] Residential – Exposures for non-porous surfaces. Exposure assumptions are for adults for 24 years, 16 hours/day, 250 days/year; exposure pathways include dermal and oral associated with hand-to-mouth activity. Inhalation exposures are not included in this evaluation. Values are provisional only.

[d] no toxicity value available to derive cleanup goal.

[e] Using only a comparison of acute lethality data (LD50), the nitrogen mustards appear to be somewhat less toxic than sulfur (distilled) mustard (HD). Therefore, the cleanup goal for HD can be used for the nitrogen mustards and would be sufficiently protective.

[f] Using only a comparison of acute lethality data (LD50), these nitrogen mustard degradation byproducts appear to be somewhat less toxic than sulfur (distilled) mustard (HD). Therefore, the cleanup goal for HD can be used for these chemicals and would be sufficiently protective.

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Table 3. Proposed Target Compounds, their Risk-Based Surface Cleanup Residential Levels, Estimated Instrument Detection Limits, and Proposed Spiking Levels

Compound Class	Compound [a]	Battelle Rationale for Selection	Risk-Based Surface Cleanup Goals – Residential (µg/cm^2)	Instrument Detection Limits [b]		Analytical Method	Spiking Levels (µg/wipe)		
				µg/mL	µg/cm^2		1x	5x	10x
CWA- Blister Agents	* Distilled Mustard (HD)	Different types of blister agents	0.000081	0.0011	0.000011	GC/HRMS-SIM	0.008	0.040	0.080
	**Mustard , nitrogen (HN-3)		0.000081 [c]	0.00002	0.0000002		0.008	0.040	0.080
CWA-Blister Agent Degradation Products	*1,4-Dithiane	Inclusion of degradation products for different CWAs	2.1	0.010	0.00010	GC/LRMS-SIM	0.040	0.200	0.400
	**Thiodiglycol (TDG)		Not Available	0.020	0.00020	LC/MS/MS	0.400	2.0	4.0
CWA- Nerve Agents	**Soman (GD1 and GD2)	Compounds with relatively low risk levels (in µg/cm^2)	0.00086	0.00009	0.0000009	GC/HRMS-SIM	0.008	0.040	0.080
	* VX		0.00013	0.0022	0.000022		0.012	0.060	0.120
CWA-Nerve Agent Precursors and Degradation Products	* Methylphosphonic acid (MPA)	Inclusion of degradation products for different CWAs	5.2	0.018	0.00018	LC/MS/MS	0.400	2.0	4.0
	**Pinacolylmethylphosphonic acid (PMPA)		Not Available	0.020	0.00020		0.400	2.0	4.0
OP Pesticides	* Dichlorvos	TEPP, a relatively unstable OP, is included to challenge the method	0.0022	0.010	0.00010	GC/LRMS-SIM	0.040	0.200	0.400
	**Tetraethyl pyrophosphate (TEPP)		0.0022 [c]	0.010	0.00010		0.040	0.200	0.400

[a] * denotes compounds designated by EPA to be included in this project and ** denotes compounds selected by Battelle.

[b] Instrument Detection Limit for each target analyte is based on a 10:1 S/N of the selected qualifier ion of the analyte by gas chromatography/low resolution mass spectrometry-selected ion monitoring (GC/LRMS-SIM), gas chromatography/high resolution mass spectrometry-selected ion monitoring (GC/HRMS-SIM), or liquid chromatography/mass spectrometry/mass spectrometry (LC-MS/MS) analysis. This assumes a wiped surface area of 100 cm^2. Final extract volume is 1 mL for GC/MS and 10 mL for LC/MS/MS.

[c] An assumption is made that compounds in the same chemical class would have similar risk-based surface cleanup goal.

Table 4. Proposed Target Compounds, their Risk-Based Surface Cleanup Residential Levels, Proposed 1x Spiking Levels, and Concentration of Spiking Solution

Compound Class	Compound [a]	Analyte Group	Risk-Based Surface Cleanup Goals – Residential (µg/wipe) [b]	Analytical Method	1x Spiking Concentration (µg/wipe)	Concentration of Target Analyte in Spiking Cocktail (µg/mL) [d]
CWA- Blister Agents	* Distilled Mustard (HD)	I	0.0081	GC/HRMS-SIM	0.008	0.008
	**Mustard , nitrogen (HN-3)	I	0.0081 [c]		0.008	0.008
CWA-Blister Agent Degradation Products	*1,4-Dithiane	II	210	GC/LRMS-SIM	0.040	0.040
	**Thiodiglycol (TDG)	III	Not Available	LC/MS/MS	0.400	0.40
CWA- Nerve Agents	**Soman (GD1 and GD2)	I	0.086	GC/HRMS-SIM	0.008	0.008
	* VX	I	0.013		0.012	0.012
CWA-Nerve Agent Precursors and Degradation Products	* Methylphosphonic acid (MPA)	III	520	LC/MS/MS	0.400	0.40
	**Pinacolylmethyl-phosphonic acid (PMPA)	III	Not Available		0.400	0.40
OP Pesticides	* Dichlorvos	II	0.22	GC/LRMS-SIM	0.040	0.040
	**Tetraethyl pyrophosphate (TEPP)	II	0.22 [c]		0.040	0.040

[a] * denotes compounds designated by EPA and ** denotes compounds selected by Battelle.

[b] Based on wiped surface of 10cm x 10 cm.

[c] An assumption is made that compounds in the same chemical class will have the same risk-based surface cleanup goal.

[d] Concentration of target analyte in single or multi-analyte spiking cocktail. To accomplish 1x spiking level, 1000 µL of each cocktail will be spiked onto test coupons

B1.3. Description of Test Coupons

Five types of test materials, namely, laminate, galvanized metal, bare wood, industrial carpet, and concrete will be evaluated. Laminate sheets (48"x 96", A'Jack Inc., Columbus, Ohio), premium eastern bare pine wood (96"x 120", Home Depot, Canal Winchester, OH), and industrial-grade carpet squares (24"x 24", Carpet Corporation of America, Rome, GA) will be purchased in bulk and cut into 6"x 6" (~15 cm x 15 cm) test coupons. The 24 gauge galvanized sheet metal (Adept Products Inc., West Jefferson, OH) and concrete which conforms to ASTM C90 (Wellnitz Company, Columbus, OH) will be purchased as pre-cut coupons in 6" by 6" size. The concrete coupons will be primed with one coat of latex primer (Kilz 2, Home Depot, Canal Winchester, OH), followed by one coat of white latex (American Tradition Interior 100% Acrylic Ultrawhite, Lowe's, Canal Winchester, OH). A 10 x 10 cm square will be marked on each coupon to indicate the spiking area (Figure 3). A scriber will be used to mark the 10 x 10 area on all surfaces except carpet. As for the carpet coupons, a 10 x 10 cm will be marked using masking tape. The 15 cm x 15 cm size coupon is a workable size for performing wiping in a fume hood and for disposal afterward.

It is anticipated that porous surfaces such as bare wood and industrial carpet will tend to absorb the spiked target analytes, and thus result in lower recoveries and poorer reproducibilities of these analytes than the non-porous surfaces (such as laminate) when wiped with IPA-wetted wipe. Painted concrete surfaces may present a challenging matrix background (especially for low-spike levels) that could impact the analysis of target analytes by the selected analytical method. The galvanized-metal surfaces may also react with selected CWAs such as VX and cause reduced recoveries of the target analyte from the surface.

B1.4. Wipes

Cotton gauze will be used as the wiping material. Cotton gauze was chosen because it is commonly used for surface wiping, easily transported, readily wetted, and convenient for sampling most surfaces. IPA is selected as the primary wetting solvent for the cotton gauzes because of its ability to dissolve the target analytes and for its low toxicity. A second wetting solvent more polar than IPA (e.g., methanol) or a combination, dual-solvent system, will be evaluated for the more polar Group III analytes.

Because the cotton gauze wipe material is known to potentially present matrix interferences, the cleanliness of the cotton gauze varies by brand and even by lot, and this effort is focused on achieving low-level risk-based surface cleanup goals under the Cleanup Scenario, the wipes will be pre-cleaned. The procedure for pre-cleaning will involve extracting them with acetone followed by dichloromethane (DCM) using accelerated solvent extraction (ASE), following the procedures used in an on-going EPA study (*8*). The pre-cleaned wipes will be dried in a drying chamber under nitrogen. Two dried and clean wipes, each wetted with 2-mL of IPA, will be placed in a clean jar. The jar containing the pre-cleaned wipe will be sealed with Teflon tape and stored in a refrigerator for up to 1 month until it is ready to use. Note that two precleaned and wetted wipes will be used for each test coupon. Wipe sampling procedure is described in Section B1.6.

The cotton gauze/IPA wiping approach may not be effective on non-porous surfaces such as industrial carpet and bare wood. In the event that the sampling method is suspected of being ineffective in recovering the target analyte(s) from the surface, Battelle will explore the modification and/or refinement of the sampling procedure to improve recoveries. If the

evaluation of a second wipe material or a third wetting solvent is necessary during the performance of this project, Battelle will discuss the related issues with the EPA TOPO and propose the alternative approach for method improvement. If necessary, a modification of the project in terms of scope, and budget will be needed to implement these changes.

B1.5. Preparation of Spiked and Non-spiked Test Coupons

As shown in Figure 2, experiments for the comparison of single analyte versus multi-analyte spiking method on the laminate surface coupons will be carried out first (Phase I). Table 5 summarizes the number of wipe samples that will be generated for the Phase I experiments. At 5x level, two types of spiking solutions will be prepared, namely single-analyte and multi-analyte in either acetone, for Groups I and II analytes, and acetone or methanol for Group III analytes. The target analytes will be purchased individually, then stock solutions will be prepared individually for single-analyte spiking and combined accordingly for multi-analyte spiking. Tables 6 and 7 summarize the number of samples that will be generated under Phase II experiments using IPA-wetted wipes and methanol-wetted wipes, respectively. Multi-analyte spiking and horizontal wiping methods are proposed for the Phase II experiments. As shown in Table 6, two spiking levels (1x and 10 x) will be used for laminate test coupons and three spiking levels (1x, 5x, and 10x) will be used for the other four types of test coupons. A different wetting solvent, methanol, will be tested with Group III analytes to determine if improved recoveries could be achieved.

All spiking procedures will be carried out in a fume hood. A group of four test coupons (3 to be used as field spikes and 1 to be used as a field blank) will be placed in a clean container inside the hood. An aliquot (1000 µL) of the spiking solution will be spiked onto each coupon at 5 spots, at a rate of 200 µL/spot (Figure 3). For each field blank, same amount of solvent (1000 µL) used for the preparation of the individual spiking solution will be spiked in the same manner as the field spike test coupons. After spiking, the coupons will be left in the hood for an additional five minutes for drying. The drying time for the spiked coupons may be adjusted as necessary, after discussion with the EPA TOPO.

Table 5. Wipe Samples to be Generated for Phase I Experiments for Multi-analyte versus Single Analyte Spiking Comparison

Target Analyte or Group	Laminate Surface							
	Sample Types and Number of Samples to be Collected in Phase I Approach – Multi-Analyte Spiking + Limited Single Analyte Spiking (5x Level) [a] Wiping Solvent Isopropyl Alcohol							
	Spiked Coupon		Non-Spiked Coupon	Post-Extraction Spikes	Spiked Wipes	Non-Spiked Wipes [f]	Solvent Spikes [a] (100% Recovery)	Total
	Horizontal Wiping	Vertical Wiping						
Group I [b]	3	2	1	1	6 [e]	1 [g]	1	12
Group II [c]	3	2	1	1	6 [e]	1 [g]	1	12
Group III [d]	3	2	1	1	6 [e]	1 [g]	1	12
GD	3	2	1	1	3	1 [h]	1	12
Dichlorvos	3	2	1	1	3	1 [h]	1	12
PMPA	3	2	1	1	3	1 [h]	1	12
Total	**18**	**12**	**6**	**6**	**27**	**6**	**6**	**81**

[a] Spiking level as defined in Table 3

[b] Group I consists of HD, HN-3, VX, and GD

[c] Group II consists of 1,4-dithiane, dichlorvos, and TEPP

[d] Group III consists of TDG, MPA, and PMPA

[e] Three of the spiked wipes for each group will be refrigerated for 48 hours along with field spike and field blank samples (Section B1.6), while the other 3 spiked wipes will be freshly prepared prior to sample extraction (Spiked wipes are defined in Section B2.4).

[f] Non spiked wipes are method blanks (as defined in Section B2.2.)

[g] Each non-spiked wipe will be stored for 48 hours along with the field spiked, field blank, and the associated spiked wipes.

[h] Each non-spiked wipe will be freshly prepared, extracted with the respective field spike and field blank samples, along with the stored wipe method spikes, wipe method blank, and freshly prepared wipe method spikes, and analyzed for all the target analytes in that group.

Table 6. Wipe Samples to be Generated Following Multi-Analyte/ Single Analyte Comparison [a] Phase II Approach – Wiping Solvent Isopropyl Alcohol

Target Analyte	Laminate Coupons[b]		Galvanized Metal Coupons		Bare Wood Coupons		Industrial Carpet Coupons		Painted Concrete Coupons		Post-Extraction Spikes [c]	Spiked Wipes [a]	Non-Spiked Wipes [g]	Total
	Spikes	**Non-Spikes**	**Spikes**	**Non-Spikes**	**Spikes**	**Non-Spikes**	**Spikes**	**Non-Spikes**	**Spikes**	**Non-Spikes**				
Group I [d]	6	1	9	1	9	1	9	1	9	1	5	9	3	64
Group II [e]	6	1	9	1	9	1	9	1	9	1	5	9	3	64
Group III [f]	6	1	9	1	9	1	9	1	9	1	5	9	3	64
Total	**18**	**3**	**27**	**3**	**27**	**3**	**27**	**3**	**27**	**3**	**15**	**27**	**9**	**192**

[a] Triplicates at spiking levels of 1x, 5x, and 10x, for each surface type, except where noted otherwise (see section B2.4). Spiking levels are defined in Table 3.
[b] Triplicates at spiking levels of 1x and 10x
[c] A single replicate for each surface type and for each Group of analytes at spiking level of 5x only (post-extraction spike is defined in Section B2.5)
[d] Group I consists of HD, HN-3, VX, and GD
[e] Group II consists of 1,4-dithiane, dichlorvos, and TEPP
[f] Group III consists of TDG, MPA, and PMPA
[g] Non spiked wipes are method blanks (as defined in Section B2.2.)

Table 7. Wipe Samples to be Generated using Methanol as a Wetting Solvent for the Polar Target Analytes [a] Phase II Approach

Target Analyte or Group	Laminate Coupons		Galvanized Metal Coupons		Bare Wood Coupons		Industrial Carpet Coupons		Painted Concrete Coupons		Post-Extraction Spikes [b]	Spiked Wipes [a]	Non-Spiked Wipes [e]	Solvent Spikes (100% Recovery) [c]	Total
	Spikes	**Non-Spikes**	**Spikes**	**Non-Spikes**	**Spikes**	**Non-Spikes**	**Spikes**	**Non-Spikes**	**Spikes**	**Non-Spikes**					
Group III [d]	9	1	9	1	9	1	9	1	9	1	5	9	3	1	68

[a] Triplicates at spiking levels of 1x, 5x, and 10x (spiked wipes are defined in section B2.4). Spiking levels are defined in Table 2.
[b] A single replicate for each surface type at spiking level of 5x only (post-extraction spike is defined in Section B2.5)
[c] A single replicate at spiking level of 5x only
[d] Group III consists of TDG, MPA, and PMPA
[e] Non spiked wipes are method blanks (as defined in Section B2.2.)

B1.6. Wipe Sampling Approach

For Phase I experiments, the spiked laminate coupons will be placed in clean trays (16" x 16" x 1") in both horizontal and vertical positions for wipe sample collection in the fume hood. Note that all experiments will be performed in the fume hood under a constant laboratory temperature (~71±5°F). The temperature will be measured with a National Institute of Standards and Technology-traceable thermometer daily while coupon spiking is occurring. The designated wiping area (10 by 10 cm) on the test coupon shown in Figure 3 will be wiped with two pre-cleaned cotton gauze pads (3" x 3"-12 ply), each wetted with 2-mL IPA. The first IPA-wetted wipe will be used to wipe the coupon area in a single direction from top to bottom, while the second wetted wipe will be used to wipe the same coupon area in a single direction from left to right, with three strokes each. After the first stroke, the exposed surface of the first cotton gauze will be folded inward for the second stroke, and then folded again for the third stroke. The cotton gauze pad is folded again with the exposed surface inside; then placed in the original jar. The test coupon will then be wiped again with the second wipe using the same procedures as described above. The second wiped cotton gauze pad will be placed in the same container as the first wiped cotton gauze pad; then the container sealed with Teflon tape and refrigerated for 48 hours prior to extraction and analysis. The purpose of this 48 hour storage time is to simulate field handling and storage conditions of the wipe samples as well as the elapsed time between sampling and extraction. Wipe samples spiked with the target analytes (Groups I, II, or III), along with non-spiked wipes, will also be stored under the same conditions as the field samples. For Phase II experiments, all spiked test coupons will be placed in the horizontal position for wiping, using the same procedures as described above. Storage conditions of Phase II samples will be determined, following discussion of Phase I results with the EPA TOPO.

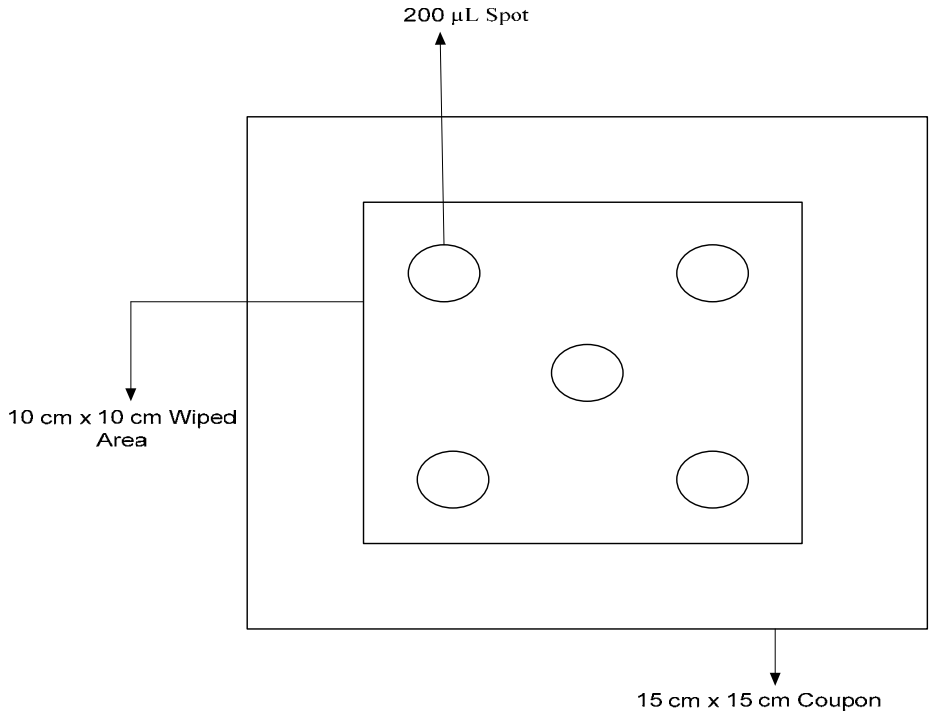


Figure 3. Spiking of Individual or Multi-Analyte Cocktail on Test Coupon

B1.7. Wipe Sample Preparation and Analysis Methods

For Groups I and II analytes, the surface wipe samples collected from spiked test coupons (i.e., field spiked samples) will be extracted with 50% DCM in acetone using Accelerated Solvent Extraction (ASE), based on the EPA Method 3545A, with minor modifications intended to enhance recoveries of the target analytes from the wipe matrix (*9*). The modifications consist of increasing static extraction cycle from one to two and the static extraction time from 5 minutes to 10 minutes. Note that each wipe storage jar will be rinsed with 50% DCM in acetone and the rinsates combined with their respective wipe sample for processing. The QC samples for each group (i.e., stored wipe method blanks, field blanks, freshly-prepared wipe method spikes, and stored wipe method spike samples) will be extracted by the same procedure as the field spiked samples. After extraction, each sample extract will be concentrated to 1 mL using Kuderna Danish (KD) evaporating technique and spiked with known amount of the internal standards. The internal standard mixture will consist of 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}, which is based on an EPA Method 8270D (*10*). The concentrated sample extracts will then be analyzed by either GC/HRMS (Group I analytes) or GC/LRMS methods (Group II analytes) based on analytical methods developed under other studies (*8*). According to the retention time of the individual target analyte, appropriate internal standard compounds will be assigned to each target analyte for quantification. Note that all 6 internal standards may not be needed for quantification. The finalized analytical methods will specify which internal standards are used. However, the other unused internal standards can provide useful information for future validation study. The final concentration for the internal standards will be 5 ng/mL for GC/HRMS analysis and 100 ng/mL for GC/LRMS analysis. Draft analytical protocols for GC/HRMS (Group I analytes) and GC/LRMS (Group II analytes) methods are included in Appendix B.

For Group III analytes, the wipe samples will be extracted with Milli-Q, deionized water using a syringe extraction procedure. The QC samples (i.e., stored wipe method blanks, field blanks, freshly-prepared wipe method spikes, and stored wipe method spike samples). Each wipe will be extracted using a total of 6 mL of water. The extract volume will be adjusted to 10 mL with Milli-Q water, then filtered. An aliquot of each extract for Group III analytes will then be spiked with the appropriate isotopically-labeled internal standard ($^{13}C_4$-TDG, $^{13}C_1$, D_3-MPA, $^{13}C_6$-PMPA) and analyzed by Liquid Chromatography (LC)-MS-MS for TDG, MPA, or PMPA, respectively, using existing protocols. Minor optimization of Battelle's current LC-MS/MS method for MPA will be required to enable the incorporation of the ^{13}C, D_3-MPA internal standard. The method optimization for MPA is described in the draft analytical protocol for the LC-MS/MS method for Group III analytes, which is included in Appendix B.

The final analytical protocol for Groups I, II, and III target analytes will be included in the final report.

B2. Field Samples and Quality Control (QC) Samples

Field spiked samples and six types of QC samples will be collected and analyzed concurrently to document data quality. The types of QC samples include (1) method blanks, (2) field blanks, (3) analytical method spiked samples, (4) post-extraction spiked sample extracts, (5) 100% recovery standard samples, and (6) performance evaluation samples.

B2.1. Field Spiked Samples

Field spiked samples (spiked coupons) will be generated from the spiked test coupons from Phase I and II experiments. One type of spiked test coupons (laminate) will be generated in Phase I and all five types of spiked test coupons (laminate, metal, concrete, bare wood, industrial carpet) will be generated in Phase II. Triplicate samples at each spiking level from each type of surface will be generated. Tables 5, 6, and 7 summarize the number of field samples to be generated. Recovery data generated from the field spiked samples will be used to evaluate overall wipe sampling method precision and accuracy.

B2.2. Method Blanks

The method blank (non-spiked wipe), which will consist of a pre-cleaned cotton gauze, will be used to determine if any contamination occurred during the analytical sample storage, preparation, concentration, and analysis procedures. The method blank will be carried through the same sample storage and preparation procedures as the field spiked and field blank samples using the same lot number of extraction solvent. Two sets of wipe method blanks will be created; one set will be stored with the field spiked samples, field blanks, and wipe method spikes (one for each group and analytical method), and another set to be freshly prepared prior to extraction of all stored samples and freshly prepared wipe method spikes (also one for each group and analytical method). Method blank result will be used to demonstrate that all glassware, reagents, and instruments are free of interferences and that the wipe material, storage, and/or sample preparation processes are not contributing a background level of each target analyte.

B2.3. Field Blanks

The field blank (non-spiked coupon) is the wipe sample collected from a non-spiked test coupon. Any potential contamination resulting from sample handling will be addressed by the field blank samples. The field blank result will be used to determine whether other chemical residues extracted on or within the wiped surface interfere with the analysis of the target analytes.

B2.4. Method Spiked Samples

The method spiked sample (spiked wipe) is a clean wipe that is spiked with known amounts of target analyte(s). Two types of wipe method spikes will be generated; one set to be refrigerated with their respective field spikes, field blank, and wipe method blank samples for 48 hours (Phase I only), and another set, freshly prepared prior to extraction. The spiked wipe is then prepared and analyzed by the same procedures as the field samples. The method spike result will be used to document effect of storage on target analytes and analytical method precision and accuracy.

B2.5. Post-extraction Spiked Field Blank Sample Extracts

The post-extraction spiked sample extract is prepared by spiking an aliquot of the field blank sample extract with the target analyte such that the concentration of target analyte in the spiked sample is at 5x. Recovery results of the post-extraction spiked field blank sample extracts will be used to document any sample matrix interference (e.g., matrix enhancement or suppression effects) and could be used as a correction factor for potential sample matrix interference.

B2.6. 100 Percent Recovery Standard Samples

The 100% recovery standard sample (solvent spike) is an aliquot of extraction solvent that is fortified with the same spiking solution used to spike method spikes. It will be used both to

evaluate the ability of the analytical system to detect the analytes and to test the spiking solution. Note that 100% recovery standard samples will only be prepared and analyzed for Phase I IPA-wetted wipes, and Phase II methanol-wetted wipes.

B2.7. Performance Evaluation Samples

Performance Evaluation (PE) samples will be prepared and analyzed in Phase I to confirm method performance, and as such the PE samples will not be repeated in Phase II. PE samples will be prepared for Groups II and III target analytes only and will be used to challenge the analytical instruments (GC/LRMS and LC/MS/MS) and to document the performance evaluation for standard preparation and analysis. The standards will be from a second source, and will be prepared in the same manner and concentration as the CCV (5x or mid point on the cal curves). The PE sample will not be available for Group I target CWAs because there is a single source for these chemicals (Edgewood Chemical and Biological Center). PE acceptance criteria will be percent difference of ± 10%. If the PE fails, the standard will be run again and a second failure will require the instrument(s) to be recalibrated. There is no SOP for preparation of PE samples since this is considered a standard laboratory dilution method.

B3. Sample Handling and Custody Requirement

The wipe samples will be generated, extracted, and analyzed in Battelle's Columbus Analytical Chemistry (CAC) laboratories The preparation of all samples will be documented in project specific laboratory record books (LRBs) to document internal sample chain-of custody. Sample transfers, retrievals, and storage will be documented in the LRBs throughout the laboratory activities, so that the location of a sample can be determined at any time. Documentation will include date and time of activity; name of person retrieving, transferring, or storing the samples; and location and conditions of storage. If not in the physical custody of the laboratory staff, samples will be returned to appropriate storage, and the storage location and conditions documented in the LRBs.

The sample codes will be assigned a unique nine-digit identification (ID) number (XXXXX-XX-XX). The first five digits of this ID number will correspond to the LRB number in which generation of the sample is being documented, the sixth and seventh digits to the page in the LRB, and the last two digits to the line on the page assigned to an individual sample. The ID number will be used in documenting all laboratory activities to reference individual samples.

The field test coupons will be decontaminated with bleach then disposed of as hazardous waste, following collection and extraction of the wipe samples. Extracted wipes will be disposed of as hazardous waste. Upon completion of the laboratory analyses, all sample extracts will be returned to archival storage (freeze at -20°C±10ºC or refrigerate at 4°C ±3ºC). The transfer to storage will be documented in the LRB. One month after the final data package of the sample set has been submitted to and accepted by the EPA, the all sample extracts will be disposed of by Battelle following established laboratory procedures, unless requested otherwise by the EPA.

B4. Inspection/Acceptance of Supplies and Consumables

The purity of all target CWAs will be checked at Battelle West Jefferson Laboratory. Dilutions of all neat CWAs at levels below RDTE (Research, Development, Testing and Evaluation) together with the purity results will be transferred to Battelle Columbus laboratory where all the experimental activities will be performed. The purity for the commercially available standards for target analytes and internal standards will be based on the Certificate of Analysis records to

be provided by vendors. Bulk materials for preparation of test coupons will be purchased from the same lot numbers. Consumables (solvents, neat chemicals, and standard solutions) will be labeled with the expiration dates suggested by the manufacturer. These expiration dates will be adhered to by the laboratory. Purity, expiration dates, and lot numbers of standards, solvents, coupons, and other consumables will be recorded in the project specific LRBs.

B5. Instrumentation Calibration and Frequency

The GC/LRMS system will be tuned with the calibration gas perfluorotributylamine (PFTBA) prior to set up of each analysis sequence following the standard instrument-specific protocol (*11*). Mass spectral intensities for PFTBA will be generated and these intensities will be used to verify that the mass tuning of the mass spectrometer has not varied significantly during analysis of the samples. The calibration results and GC/LRMS maintenance records will be kept in the GC/LRMS facility LRBs.

The GC/HRMS system calibration will be accomplished using perfluorokerosene (PFK). The manufacturer supplied software will be utilized to calibrate the mass analyzer with the accurately known exact masses of PFK ions produced in the source. Instrument sensitivity tuning of the GC/HRMS system will be completed using an appropriate reference (lock-mass) compound (e.g., PFTBA, PFK, decalin-d_{18}, etc.).

Instrument sensitivity of the GC/HRMS system will be optimized using the auto-tune program supplied by the manufacturer (*12*). Once the source sensitivity optimization is complete, the slits will be adjusted to achieve the desired resolving power (e.g., $R \geq 10{,}000$ when measured at 10% peak valley). Results of the auto tune program and complete instrument settings prior to each acquisition will be printed and included in the data package. Also included will be printouts (oscilloscope captures) of the lock mass and calibration mass ions at both the beginning and ending of the data of record acquisition to demonstrate appropriate instrument resolving power.

The LC-MS-MS system will be mass-calibrated, in accordance with the manufacturer specifications (*13*), prior to sample analysis by infusing Poly Ethylene Glycol (PEG) 400 solution in Electrospray ionization (ESI) Positive mode to assure that the proper mass-to-charge ratios (m/z) have been assigned. The first quadrupole mass analyzer (MS1) and the second quadrupole mass analyzer (MS2) are tuned between 40-400 m/z. The mass accuracy after mass calibration is performed should be ±0.2 Da.

For each analysis sequence and each analysis group, multi-point calibration curves (0.5x, 1x, 5x, 10x, and 15x; relative to the 1x spiking level, as defined in Table 3) which include target analytes and internal standard(s) will be generated. Calibration standard solutions consist of target analytes and internal standards. In addition, for GC/HRMS, 1,4-dithiane and 1,4-thioxane will be monitored during the analysis of wiped surfaces or wipe samples spiked with Group I target analytes. For GC/LRMS and GC/HRMS, an average response factor (RF) method will be used for the quantification, if the % RSD of the RF values for the target analyte is ≤ 15%. If %RSD is > 15%, regression (either linear fit or quadratic fit, depending on the best curve fit) method will be used. If regression method is used, the correlation coefficient (r) will be greater than 0.99. For LC-MS-MS analysis, the recalculated concentrations of the standards used to generate each calibration curve should be within 15 percent of the theoretical value for that standard, except in the case of the lowest standard (0.5x), which may be within 25 percent. The calibration curves will be linear, with coefficient of determination (r^2) >0.99 and with the origin

excluded. One of the calibration points other than the 1x may be dropped if needed to meet these requirements.

For GC/LRMS, GC/HRMS, and LC-MS-MS, a solvent analysis (system blank) will be performed after the injection of the highest level of the standard solution (15x) to document that there is no carry over from the instrument. A mid-level standard solution (5x) will be used as the continuous calibration verification (CCV) solution and will be analyzed after every 10 samples. Each analysis sequence will end with a CCV and a sensitivity check standard (the 1x standard) to document the performance of the instrument. The percent deviation will be within ±25% for each target analyte in the CCV as compared to the expected values.

If CCV values fail the acceptance criteria, corrective actions will be implemented accordingly. The corrective actions may include cleaning MS source, cutting the front end of a GC column, changing gold seal and injector inlet, changing GC or LC column.

B6. Instrument Maintenance

Preventive maintenance will be performed on GC/LRMS, GC/HRMS, and LC-MS/MS systems according to the schedule defined in the appropriate facility standard operating procedures (SOPs). Preventive maintenance and calibration will also be conducted on micropipettes and balances, according to the schedule specified by the manufacturers and as defined by the established laboratory procedures. As for refrigerators and freezers, the temperature of each unit is checked and recorded daily to ensure that it is within the specified range (4°C - 7°C for refrigerators and -20°C±10°C for freezers). If the temperature does not meet the specifications, even after minor adjustments, the refrigerator or freezer will be serviced and in extreme cases replaced. In addition, the temperature of each unit in Battelle's RDTE analytical laboratories will be recorded continuously using a temperature data logger, and the data downloaded to a PC and evaluated once every 3 months. When applicable, the following information will be recorded:

- Results of performance tests
- Instrument calibration information and calibration checks
- Dates on which routine maintenance is performed and a detailed account of what was done
- Instances of instrument failure
- Record of all changes in location, instrument repairs, changes, and modifications
- Description of any problems encountered and steps taken to rectify them.

C
Data Management

A variety of records will be generated for this project. The records will include the TQAP, LRBs, electronic files (both raw data and spreadsheets of sample results or statistical calculations), and the final project report. This section will describe how the project records will be generated, compiled, reviewed, maintained, reported, and archived.

C1. Documentation/Records

All preparation and analysis activities will be recorded in LRBs. Data will be generated by GC/LRMS, GC/HRMS, or LC/MS analysts. All data will be electronically transferred by analysts to validated Excel spreadsheets. All data will be thoroughly reviewed first by analysts then by the appropriate Battelle TLs.

Data packages will include any of the following elements that are applicable to the analysis:

- Instrument tuning (GC/LRMS, GC/HRMS, and LC/MS methods)
- Calibration data
- Calibration verifications
- Internal standard response and retention times (GC/MS methods)
- All QC data required by the analytical method or the TQAP
- Run logs
- Recovery data for field spiked and QC samples.

All records received by the Battelle TLs will be maintained in the Battelle TL's office until the completion of the report at which time the records will be transferred to permanent storage at Battelle's Records Management Office. All Battelle LRBs are stored indefinitely, either by Battelle's Records Management Office or the Battelle TLs. One month after the final report is approved by the EPA TOPO, all files associated with the test including project management files and the draft data summary, will be sent to Battelle's Records Management Office and archived for at least three years. EPA will be notified before disposal of any files.

All written records must be in ink. Any corrections to notebook entries, or changes in recorded data, must be made with a single line through the original entry. The correction is then to be entered, initialed, reason for the change, and dated by the person making the correction.

C2. Data Analysis

The following section describes the data analysis to be performed. Any calculations done in addition to those discussed below will be described in detail in the final report.

C2.1. Accuracy

Accuracy is a measure of how close the measurements are to spike values. The analytical method accuracy will be reported as percent recovery from the spiked samples using the following equation:

$$\% \text{ Recovery} = \frac{C_m - C_\mu}{C_s} \quad x\,100$$

where C_m, C_μ, and C_s are the concentration of each target analyte measured in the spiked sample, in the un-spiked sample, and the spike concentration, respectively. Analytical method accuracy and overall sampling and analysis accuracy will be calculated in this manner.

C2.2. Precision

Precision is the reproducibility of the replicate measurements. The standard deviation (S) of the results for the replicate analyses of the same sample will be calculated as follows:

$$S = [\frac{1}{n-1}\sum_{k=1}^{n}(M_k - \overline{M})^2]^{1/2}$$

where n is the number of replicate samples, M_k is the measurement for the kth sample, and $\overline{M}$ is the average measurement of the replicate samples. The precision for each sample will be reported in terms of the percent relative standard deviation (RSD), which will be calculated as follows.

$$RSD(\%) = \left|\frac{S}{\overline{M}}\right| \times 100$$

Analytical method precision and overall sampling and analysis precision will be calculated. Comparisons of method performance will be reported as percent difference (%D) between the field spiked samples generated by the two types of methods.

$$\% \ D = \frac{C_1 - C_2}{C_{avg}} \quad x\,100$$

where C_1 and C_2 are the concentrations of the mean values of the target analyte measured from replicate samples in the single- and multi-analyte spiking and/or horizontal and vertical wiping methods, respectively; C_{avg} is the average of C_1 and C_2.

Analytical and overall method precision will be documented in term of %RSD values in triplicate method spiked and field spiked samples, respectively. Method comparisons will be expressed as %D between the two methods employed. In Phase I experiments, two spiking (single- vs. multi-analyte) and two wiping (horizontal vs. vertical) methods will be evaluated. Comparisons of the method performance between each of the two methods evaluated will be expressed as % D values of the mean values derived from the triplicate samples generated from the two methods evaluated.

C2.3. Evaluation of Data Quality Objective Goals

The criteria for Phase I method performance is set at ±10% D values for the results obtained between single- versus multi-analyte spiking, and horizontal versus vertical wiping methods. Phase I criteria must be met in order for Battelle to proceed with Phase II. If one or more target analytes fail Phase I criteria, then Battelle will contact the TOPO immediately to discuss the implications and the course of action for the rest of the project.

Data quality objectives for the measurement data resulting from the project will be expressed in terms of precision and accuracy goals. Analytical method precision and accuracy will be monitored through the analysis of QC samples (i.e., wipe method spikes). The data quality objective goals for the analytical method are at ≤ 10% for analytical method precision (%RSD of the triplicate method spikes) and 80-105% (% recovery of method spikes) for analytical method accuracy.

The data quality objectives for the wipe sampling method(s) to be established under this project, which are inclusive of the analytical method data quality objectives, are summarized in Table 8. The focus of this project is to evaluate the wipe sampling method and document the performance of the method. As indicated in Section B above, non-porous surfaces such as laminate are expected to provide relatively higher recoveries (accuracy) and tighter reproducibility (precision) of target analytes than non-porous surfaces (bare wood and industrial carpet). These expectations are reflected in the overall method performance for the various surfaces in the table below. At the completion of Phase II, Battelle will determine which target analytes meet the goals, exceed the goals and do not meet the goals for each type of test coupon. Battelle will discuss the results with EPA TOPO and determine if additional experiments would be needed under a modification of the project.

Table 8. Data Quality Objective Goals for the Wipe Sampling Method(s)

Surface Type	Data Quality Objective Goal	
	Wipe Sampling Method	
	Precision[a]	Accuracy[b]
Laminate	≤20%	70-110%
Metal	≤20%	70-110%
Painted Concrete	≤30%	30-70%
Bare wood	≤30%	30-70%
Industrial Carpet	≤30%	30-70%

[a] Wipe sampling method precision is the average %RSD values of triplicate field spiked samples

[b] Wipe sampling method accuracy is the average % recovery data of field spiked samples.

C3. Reporting

The data obtained in the project will be compiled in an EPA report. The report will describe the purpose of the project, a summary of the experimental design, the interpretation of the data, and the conclusions. The report will also contain a wipe sampling method as an appendix. A draft of the wipe sampling method will be delivered to EPA by June 23, 2008. Deviations from the TQAP will be noted in the report. The report will be approximately 30 pages.

A draft report will be submitted for review by the EPA TOPO, EPA Quality Manager, and peer reviewers. Comments on the draft report will be addressed in revisions of the report. The peer review comments and responses will be tabulated to document the peer review process. A final report will be delivered to EPA no later than September 30, 2008.

D
Health and Safety

D1. Special Facilities

Battelle is certified to work with chemical surety material through a Bailment Agreement with U.S. Army Research, Development, and Engineering Command. The Army regularly sends an Inspector General team to conduct on-site chemical surety inspections, thereby ensuring that Battelle is operating in accordance with the terms of the Bailment Agreement.

Battelle facilities available for the project are in compliance with all applicable Federal, state, and local laws and regulations, including U.S. Army regulations. Battelle's facilities meet or exceed all requirements for the safe use, storage, decontamination, and accountability of chemical agent as defined by Army regulation AR50-6. Battelle's CAC (RDTE dilute) Laboratory and Hazardous Material Research Center (HMRC) (neat and RDTE dilute) are certified by Underwriters Laboratory, Inc., in accordance with ISO 9001-2000.

D2. Staff Training and Health

Each staff member working with RDTE solutions is required to take monthly RDTE quizzes, and an annual refresher RDTE training. Prior to working with RDTE solutions, all staff members are required to read and sign off on all relevant CAC RDTE and facility SOPs (*14*) as well as the Chemical Hygiene Plan (*15*) and Physical Security Plan (*16*), then annually or every time these SOPs are revised. All staff members working with RDTE solutions are also required to have an annual physical exam with a physician on site, and once every three years during this visit a blood sample is withdrawn to monitor the background cholinesterase level.

D3. Standard/Test Sample Handling

All handling of test items, spiking solutions of contaminants and possible interferences will be done inside of a laboratory fume hood with hood sash set to the lowest height that still allows for safe manipulation of materials. All CAC RDTE spiking solutions are stored in a limited access freezer which is locked at all times and only accessed by authorized personnel on the day of spiking. The following guidelines will be adhered to:

- Personal protective equipment will include safety glasses with side shields, a fully-fastened laboratory coat, and nitrile laboratory gloves. Gloves shall be changed every 5 minutes during which RDTE solutions are being handled inside the hood and immediately changed if they become contaminated.
- All contaminated wastes will be decontaminated with the appropriate decontamination solution (e.g., 5.25% bleach) in accordance with RDTE SOPs and handled as hazardous waste and disposed of according to facility regulations.

D4. Sample Handling During Test

Laboratory and field handling of any solutions used during the test will be accomplished by taking the following precautions:

- All containers shall be stored and transported in double containment.
- Safety goggles, nitrile gloves with long cuffs, and a chemical resistant laboratory coat shall be worn when handling all chemicals. Gloves shall be immediately changed if they become contaminated.
- All CAC RDTE spiking solutions are single use only and will be decontaminated with bleach immediately at the conclusion of the spiking session of the test coupons.

E References

1. U.S. Environmental Protection Agency, 2007. *A Literature Review of Wipe Sampling Methods for Chemical Warfare Agents and Toxic Industrial Chemicals.* EPA/600/R-07/004. National Exposure Research Laboratory, Las Vegas, NV (January 2007).
2. U.S. Homeland Security Department: *National Preparedness Guideline*, September, 2007. http://www.dhs.gov/xlibrary/assets/National_Preparedness_Guidelines.pdf.
3. The Contaminants of Potential Concern (COPC) Committee of the World Trade Center Indoor Air Task Force Working Group, May 2003. *World Trade Center Indoor Environment Assessment: Selecting Contaminants of Potential Concern and Setting Health-Based Benchmarks*, www.epa.gov/WTC.
4. McKean, D.L. and Sonich-Mullin, C. *Risk-based Cleanup Goals for Indoor Surfaces, International Workshop on Decontamination of Buildings and Facilities after Chemical Terrorism, Moscow, Russia,* 2006.
5. U.S. Environmental Protection Agency, January 2006. *Quality Management Plan National Homeland Security Research Center Technology Testing and Evaluation Program (TTEP),* Version 2.
6. American Society for Testing and Materials, 2001. D6661-01 Standard Practice for Field Collection of Organic Compounds from Surfaces Using Wipe Sampling, May 2006. *Annual Book of Standards*. Vol. 11.04.
7. Bernard, C.E. Berry, M.R. Wymer, L.J. Melnyk, L.J. *Sampling Household Surfaces for Pesticides: Comparison between a Press Sampler and Solvent-Moistened Wipes,* Sci. of Total Environ. In press, 2008.
8. U.S. Environmental Protection Agency, 2006. *Evaluation of Sample Preparation and Analytical Methodologies,* Work Plan and Quality Assurance Project Plan for the Scientific, Technical, Research, Engineering, and Modeling Support (STREAMS) Contract (#EP-C-05-057), Task Order 1.
9. US EPA Method 3545A, Pressurized Fluid Liquid Extraction (PLE), Revision 1 (January 1998).
10. US EPA Method 8270D, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 4 (Feb 2006).
11. Hewlett Packard 5973 Mass Selective Detector Hardware Manual, Manual Part Number G2589-90001, Agilent Technologies (November 1999).

12. High Resolution Mass Spectrometer 119_5600_DFS_Operating Manual. Version #2.0.1.0468 Draft 1195600. Thermo Electron Corporation (June 2006).

13. "Micromass Quattro II Mass Spectrometer User's Guide," Issue 2, and "Waters Micromass Quattro Premier Mass Spectrometer Operator's Guide", Revision B.

14. Guidelines for Managing a Research, Development, Testing, and Evaluation (RDTE) Dilute Solution Laboratory – September 2005, Edgewood Chemical and Biological Center (ECBC) – Risk Reduction Office

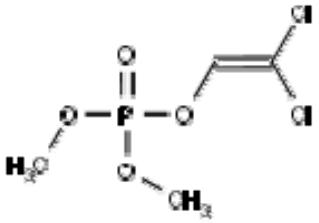
15. Chemical Hygiene Plan for the Columbus Analytical Chemistry Group (October 2007).

16. Physical Security Plan (PSP) for the Battelle Columbus Analytical Chemistry (CAC), Research, Development, Test & Evaluation (RDTE) Solution Laboratory (April 2007).

Appendix A

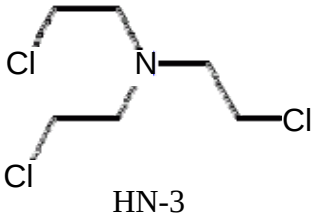
CHEMICAL STRUCTURES FOR THE COMPOUNDS OF INTEREST

1,4-Dithiane

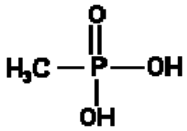


Dichlorvos

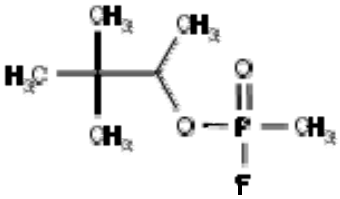
Distilled Mustard (HD)



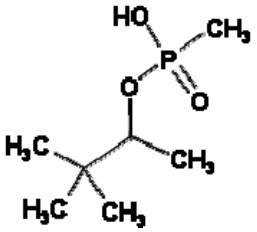
HN-3



Methylphosphonic acid (MPA)

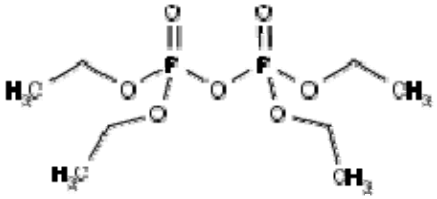


Soman (GD)

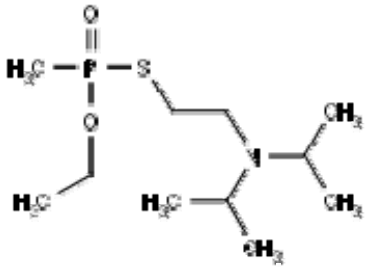


Pinacolylmethylphosphonic acid (PMPA)

Thiodiglycol



Tetraethyl pyrophosphate (TEPP)



VX

Appendix B

DRAFT GC-HRMS/SIM, GC-LRMS/SIM, AND LC-MS/MS ANALYTICAL PROTOCOLS FOR TARGET ANALYTES

Scope and Applicability

This protocol describes the general procedures implemented at Battelle Columbus for the determination of 1,4-Dithiane, GD, HD, HN-3, 1,4-Thioxane, and VX by Gas Chromatography (GC) High Resolution Mass Spectrometry. A subset of isotopically labeled polycyclic aromatic hydrocarbons (PAHs) used as internal standards in EPA Method 8270D will be used as internal standards in this analytical protocol. The methodology has yet to be validated; procedures herein may be modified prior to the start of test sample analysis.

Analytical Procedure

Reagent Preparation

Gas Chromatography

Helium: Ultra-high purity.

High Resolution Mass Spectrometry

Perfluorotetrabutylamine (PFTBA): Mass spectrometry tuning grade or equivalent.

Standards and Test Sample Preparation

Intermediate and Calibration Standard Solutions

1,4-Dithiane (DITH) Working Standard Solution (40 µg/mL): Dilute 400 µL of 1,4-dithiane stock solution (Cerilliant, 1000 µg/mL solution in methanol) to 10 mL final volume with acetone. Solution is stored in a freezer for up to 6 months.

O-Pinacolyl methylphosphonofluoridate (GD, Soman) Working Standard Solution (8.0 µg/mL): Dilute appropriate volume of GD RDTE stock solution to 10 mL final volume with acetone. Solution is stored in a freezer for up to 6 months.

Bis(2-chloroethyl) sulfide (HD) Working Standard Solution (8.0 µg/mL): Dilute appropriate volume of HD RDTE stock solution to 10 mL final volume with acetone. Solution is stored in a freezer for up to 6 months.

Tris(2-chloroethyl)amine (HN-3) Working Standard Solution (8.0 µg/mL): Dilute appropriate volume of HN-3 stock solution to 10 mL final volume with acetone. Solution is stored in a freezer for up to 6 months.

1,4-Thioxane (THIOX) Working Standard Solution (8.0 µg/mL): Dilute appropriate volume of THIOX stock solution to 10 mL final volume with acetone. Solution is stored in a freezer for up to 6 months.

O-Ethyl S-2-diisopropylaminoethyl methyl phosphonothiolate (VX) Working Standard Solution (12 µg/mL): Dilute appropriate volume of VX RDTE stock solution to 10 mL final volume with acetone. Solution is stored in a freezer for up to 6 months.

Calibration Curve Standard Solutions: Prepare separate calibration curve standards as shown in Table B-1 using a solvent system composition consistent with the final field sample extracts. Store refrigerated. Solutions are stable for 1 month.

Table B-1. Calibration Curve Solutions

Calibration Level (CL)	Volume of Working Standard Solution (µL)	Final Volume (mL)	DITH Conc (ng/mL)	GD Conc (ng/mL)	HD Conc (ng/mL)	HN-3 Conc (ng/mL)	THIOX Conc (ng/mL)	VX Conc (ng/mL)
C1 (IDL)	5	10	20	4	4	4	4	6
C2	10	10	40	8	8	8	8	12
C3	25	10	100	20	20	20	20	30
C4	50	10	200	40	40	40	40	60
C5	100	10	400	80	80	80	80	120
C6	150	10	600	120	120	120	120	180

Internal Standards

Semivolatile Internal Standard Mix (EPA Method 8270D) Intermediate Internal Standard Solution (IISS): Stock Internal Standard (IS) Mix (Supelco, 2000 µg/mL solution in methylene chloride/benzene) contains each of the following isotopically labeled analytes: Acenaphthene-d_{10}, Chrysene-d_{12}, Naphthalene-d_8, perylene-d_{12}, Phenanthrene-d_{10}, 1,4-Dichlorobenzene-d_4. Dilute 100 µL of the Stock IS Mix (2000 µg/mL) to 10 mL with acetone (pesticide residue grade). The concentration of this solution is 20 µg/mL. Solution is stored in a freezer for up to 6 months.

Semivolatile Working Internal Standard (WIS): Dilute 50 µL of the Intermediate Internal Standard Solution (20 µg/mL) to 10 mL in acetone. This will produce a WIS solution with a concentration of 100 ng/mL. Solution is stored in a freezer for up to 6 months.

Test Samples

Following extraction and concentration of sample extracts to 1 mL, each Field Spike, Field Blank, Method Blank, and Method Spike test sample extract will be fortified with 50 µL of the WIS. The sample extract will be mixed and transferred to a GC vial for

subsequent GC/HRMS analysis. The 100% Recovery Standard sample (1 mL) will also be fortified with 50 µL of the WIS. The post-extraction spiked field blank sample extract will be prepared by removing an aliquot (500 µL) of the field blank sample extract to another GC vial and adding an aliquot (2.5 µL) of the working analyte standard for GC-HRMS analysis. The concentration of the target analyte in the post-extraction spiked field blank sample extract will be at the C4 level.

Instrument Operation

The GC/HRMS system will be tuned according to the manufacture's instructions in order to verify that acceptable performance criteria are achieved. For sensitivity, the spectrometer will be tuned using either autotune or manual tune. Typically, PFTBA is bled into the instrument through the reference inlet system. When using autotune, the final optimization should show an intensity change of ± 5% relative to the previous attempt. The resolving power (m/Δm, 5% peak height) will be adjusted to ≥10,000 and documented for all lock and calibration masses in each scan function prior to the start of the analysis. Likewise, the ending resolving power must be ≥9,000 and must be documented.

At a minimum, two ion transitions (quantitation and qualifier ions) will be monitored for each target analyte. The exact mass of each monitored ion (precursor or fragment), as calculated on the HRMS data acquisition system, will be used in the acquisition method. The analytical response (peak area and/or height) will be determined. The ratio of the analytical response of the two ion transitions will be calculated. Prior to the start of the analytical sequence, the scan window time functions will be set and verified using a calibration standard of an appropriate concentration.

All chromatographic peaks must have signal-to-noise ratio ≥3 to be considered detected.

Typical GC-HRMS Operating Conditions

Typical GC/HRMS operating conditions are listed in Table B-2. Other conditions may be used but all minimum performance criteria must be met.

Table B-2. Typical GC/HRMS Operating Conditions

GC/HRMS System	Thermo Fisher DFS (or equivalent)
Gas Chromatograph	Thermo Fisher Trace GC Ultra (or equivalent)
Mass Spectrometer	Thermo Fisher DFS High Resolution Mass Spectrometer (or equivalent)
MS Source	Electron impact, positive ion mode
GC Column	Varian CP-Sil 5CB, 30 m, 0.25 mm ID, 1.0 µm film
GC Temperature Program	50 °C hold for 2.0 min 20 °C/min to 80 °C, hold for 3.0 min 4 °C/min to 250 °C, hold for 0 min 30 °C/min to 300 °C, hold for 3 min.
Carrier Gas Flow Rate	1 to 2 mL/min
Transfer Line Temperature	250 °C
Injection Volume	2.0 µL
Injection Type	Splitless (Split at 1.0 min at 30 mL/min)
Acquisition Mode	Multiple ion detection (MID), equivalent to SIM
Run Time	~55 min
Ionization Energy	30 to 70 eV
Dwell Time	25 ms for Lock and Cali Mass, ≥50 ms for analyte
Ion Source Temperature	250 °C
Trap Current	600 µA

Monitored Ions

Ions typically monitored for the target analytes are shown in Table B-3. The exact masses will be calculated using the system's data processing software. Other ions may be added or substituted to these but the elemental composition must be known and documented. Regardless of the ions monitored, all performance criteria must be met.

Table B-3. Elemental Compositions for Ions Typically Monitored by GC/HRMS

Analyte	Elemental Composition (nominal *m/z*)
DITH	$C_2H_4S_2$ (92); $C_4H_8S_2$ (120)
GD	CH_5PO_2F (99); $C_3H_8PO_2F$ (126)
HD	$C_3H_6S^{35}Cl$ (109); $C_3H_6S^{37}Cl$ (111)
HN-3	$C_5H_{10}N^{35}Cl_2$ (154); $C_5H_{10}N^{35}Cl^{37}Cl$ (156)
THIOX	C4H8SO (104); C3H6S (74)[1]
VX	$C_7H_{16}N$ (114); $C_8H_{17}N$ (127)
1,4-Dichlorobenzene-d_4 (IS)	$C_6D_4{}^{35}Cl_2$ (150); $C_6D_4{}^{35}Cl^{37}Cl$ (152)
Acenaphthene-d_{10} (IS)	$C_{12}D_9$ (162); $C_{12}D_{10}$ (164)
Chrysene-d_{12}	$C_{18}D_{10}$ (236)[2]; $C_{18}D_{12}$ (240)
Naphthalene-d_8	$C_{10}D_6$ (132)[2]; $C_{10}D_8$ (136)
Perylene-d_{12}	$C_{20}D_{10}$ (260)[2]; $C_{20}D_{12}$ (264)
Phenanthrene-d_{10}	$C_{14}D_8$ (184)[2]; $C_{14}D_{10}$ (188)

1. Secondary ion (*m/z* 74) for THIOX is optional due to large mass range ratio.
2. Secondary ion for internal standard is optional.

Quality Control

System Blanks

A system blank, prepared using a solvent system composition consistent with the final field sample extracts and spiked with the IS, will be analyzed at the beginning of the analysis to confirm system cleanliness.

A system blank will also be analyzed after the highest calibration standard; if analyte carryover ≥ 0.5× C1 level exists, a second system blank will be analyzed before test samples are analyzed. Analyte carryover will be calculated and noted in the data package.

Calibration curves

A set of calibration curve solutions will be analyzed at the start of each test sample batch. The calibration curve for each target analyte will be constructed by plotting the relative response of the quantitation ion of each analyte with respect to its internal standard (Acenaphthene-d_{10}, Chrysene-d_{12}, Naphthalene-d_8, perylene-d_{12}, Phenanthrene-d_{10}, or 1,4-Dichlorobenzene-d_4) against the concentration of the target analyte. The recalculated concentrations of the standards used to generate each calibration curve should be within 15% of the theoretical value for that standard, except in the case of the lowest standard, which may be within 25%. The calibration curves should be linear, with coefficients of determination ≥ 0.99, with the origins excluded. Weighted models may be applied but any

activity must be noted in the data package. One of the calibration points, other than the C1 standard, may be excluded if needed to meet these requirements.

Continuing Calibration and Verification (CCV) standards

A standard at C3 concentration level will be analyzed at least every 10 test samples and at the end of the analytical sequence. The concentration of the target analyte should be ± 25% of the theoretical concentration. Both ion transitions should be detected.

If a CCV fails the ± 25% accuracy criterion, all samples between the previous successful laboratory check standard and the next successful laboratory check standard must be reanalyzed.

Ion Ratios

Ion ratios will be determined using the average ratio of all calibration standards (≥C2) used in the analysis sequence.

Sensitivity check standards

A sensitivity check standard at C1 level will be analyzed near the end of the sequence. Both ion transitions should be detected with a signal-to-noise ratio ≥3.

Test Sample Concentrations Outside Calibration Curve Range

If a target analyte is detected in a test sample and the concentration is below 0.5× C1 level, the concentration will be flagged as estimated. If a target analyte is detected and the concentration is at or above 0.5× C1 level, then the actual concentration will be reported.

If the concentration of a target analyte in a test sample exceeds the upper calibration limit, the sample will be diluted and reanalyzed to bring the concentration within the calibration range.

Reporting

The analyst will assemble a data package containing the date of analysis, instrument identity, and quantitative results. Excel spreadsheets will be used to determine precision results. A brief report that discusses the analytical results and any anomalies will be provided.

Sample Disposal

Following analysis, data review, reporting, and acceptance of the analytical results, any remaining aqueous sample extracts from a given trial will be decontaminated with bleach.

Scope and Applicability

This protocol describes the general procedures implemented at Battelle Columbus for the determination of 1,4-dithiane, dichlorvos, and tetraethylpyrophosphate (TEPP) in organic solutions by gas chromatography/mass spectrometry (GC/MS). A subset of isotopically labeled polycyclic aromatic hydrocarbons (PAHs) used as internal standards in EPA Method 8270D will be used as internal standards in this analytical protocol. The methodology is yet to be finalized; procedures herein may be modified prior to the start of test sample analysis.

Analytical Procedure

Standard Solutions and Test Sample Extract Preparation

Intermediate and Calibration Standard Solutions

1,4-Dithiane Working Standard (10 µg/mL): Dilute 100 µL of 1,4-dithiane stock solution (Cerilliant, 1000 µg/mL solution in methanol) to 10 mL final volume with acetone. Solution is stored in a freezer for up to 6 months.

Dichlorvos Working Standard (10 µg/mL): Dilute 100 µL of dichlorvos stock solution (Cerilliant, 1000 µg/mL solution in methanol) to 10 mL final volume with acetone. Solution is stored in a freezer for up to 6 months.

TEPP Working Standard (10 µg/mL): Dilute 100 µL of TEPP stock solution (Absolute Chemical, 1000 µg/mL solution in hexane) to 10 mL final volume with acetone. Solution is stored in a freezer for up to 6 months.

Calibration Curve Standard Solutions: Prepare separate calibration curves as Table B-4 below using IPA as diluent. Store refrigerated. These solutions are stable for 1 month.

Internal Standards

Working EPA Method 8270D Internal Standard (WIS): Dilute 50 µL of EPA Method 8270D internal standard stock solution (Supelco, 2000 µg/mL solution in 1: 1 mixture of dichloromethane/benzene) to 10 mL final volume with acetone. Stock Internal Standard

(IS) Mix contains each of the following isotopically labeled analytes: Acenaphthene-d_{10}, Chrysene-d_{12}, Naphthalene-d_8, perylene-d_{12}, Phenanthrene-d_{10}, and 1,4-Dichlorobenzene-d_4. The final concentration for the WIS is 10 µg/mL. Solution is stored in a freezer for up to 6 months.

Table B-4. Calibration Curve Standard Solutions

Cal Std ID	Volume of Working Analyte Standard (µL)	Volume of Working Internal Standard[a] (µL)	Final Volume (mL)	1,4-Dithiane Conc (ng/mL)	Dichlorvos Conc (ng/mL)	TEPP Conc (ng/mL)
C1 (or IDL)	20	100	10	20	20	20
C2	40	100	10	40	40	40
C3	100	100	10	100	100	100
C4	200	100	10	200	200	200
C5	400	100	10	400	400	400
C6	600	100	10	600	600	600

[a] See Section 2.1.2 for the preparation of working internal standard solution.

2.1.3 Test Sample Extracts

Following extraction and concentration of sample extracts to 1 mL, each Field Spike, Field Blank, Method Blank, and Method Spike test sample extract will be fortified with 10 µL of the WIS. The sample extract will be mixed and transferred to a GC vial for subsequent GC/MS analysis. The 100% Recovery Standard sample (1 mL) will also be fortified with 10 µL of the WIS. The post-extraction spiked field blank sample extract will be prepared by removing an aliquot (500 µL) of the spiked field blank sample extract to another GC vial and adding an aliquot (10 µL) of the working analyte standard for GC/MS analysis. The concentration of the target analyte in the post-extraction spiked field blank sample extract will be at the C4 level.

Instrument Operation

Automated Hewlett-Packard gas chromatograph/mass selective detector (6890/5973A GC/MSD) equipped with an autosampler or equivalent GC/MS system. The instrument will be operated in the full mass scan (FMS) mode first to establish parameters (e.g., dwelling times for monitored ions, times for switching monitored ions) to be used in the selected ion monitoring (SIM) mode. In the SCAN mode, the detector scans all masses repeatedly during the GC run between a lower and an upper mass limit, typical from 35 to 550 atomic mass unit (amu). A project specific acquisition method for the SIM mode will be established according to the retention time and mass spectral information from the FMS mode. All calibration standards and sample extracts will be analyzed in the SIM mode. Peaks must have signal-to-noise ratios $\geq$ 3:1 to be considered detected.

The GC/MS system must be tuned according to the manufacturer's instructions, to verify that acceptable performance criteria are achieved. If the tune criteria are not met, corrective actions will take place immediately (e.g., clean MS source, change GC column, etc.).

Typical GC-LRMS Operating Conditions

Typical GC/LRMS operating conditions are listed in Table B-5. Other conditions may be used but all minimum performance criteria must be met.

Table B-5. Typical GC/LRMS Operating Conditions

GC/LRMS System	Hewlett-Packard GC/MSD(or equivalent)
Gas Chromatograph	Hewlett-Packard 6890(or equivalent)
Mass Selective Detector	Hewlett-Packard 5973A (or equivalent)
MS Source	Electron impact mode
GC Column	RTX-5MS GC column, 0.25 mm x 30 m with 0.25 µm film thickness
GC Temperature Program	100 °C hold for 2.0 min 8 °C/min to 290 °C, hold for 10 min.
Carrier Gas Flow Rate	1 to 2 mL/min
Injector Temperature	270 °C
Transfer Line Temperature	290 °C
Injection Volume	1.0 µL
Injection Type	Splitless (Split at 1.0 min at 30 mL/min)
Acquisition Mode	Multiple ion detection (MID), equivalent to SIM
Run Time	~36 min
Ionization Energy	70 eV
Dwell Time	≥50 ms for target analytes and ≥30 ms for internal standards
MS Source Temperature	230 °C

Monitored Ions

Ions typically monitored for the target analytes are shown in Table B-6. The monitored ions may be changed as necessary and will be recorded in the final protocol.

Table B-6. Ions for Target Analytes/IS Typically Monitored by GC/LRMS

Analyte	Monitored Ions (*m/z*)
1,4-Dithiane	120, 61, 46
Dichlorvos	220, 185, 145, 109
TEPP	263, 235, 179, 161
1,4-Dichlorobenzene-d_4 (IS)	152
Acenaphthene-d_{10} (IS)	164
Chrysene-d_{12}	240
Naphthalene-d_8	136

Perylene-d_{12}	264
Phenanthrene-d_{10}	188

Quality Control

System Blanks

A system blank (IPA) fortified with the IS will be analyzed at the beginning of the analysis to confirm system cleanliness.

A system blank will also be analyzed after the highest calibration standard; if carryover above 0.5× C1 level exists, a second system blank will be analyzed before test samples run.

Calibration curves

A set of calibration curve solutions will be analyzed at the start of each test sample batch. The calibration curve for each target analyte will be constructed by plotting the relative response of the quantitation ion of each analyte with respect to its internal standard (Acenaphthene-d_{10}, Chrysene-d_{12}, Naphthalene-d_8, perylene-d_{12}, Phenanthrene-d_{10}, or 1,4-Dichlorobenzene-d_4) against the concentration of the target analyte. The calibration curves can be generated using an average response factor (Rf) method, if the % RSD of the Rf values for the target analyte is ≤ 15%. If %RSD is > 15%, regression (either linear fit or quadratic fit, depending on the best curve fit) method will be used. If regression method is used, the correlation coefficient (r) should be greater than 0.99. If these criteria are not met, the GC/MS system will be checked to determine the sources for this variation. Corrective actions (e.g., clean source or change column) will be taken and all samples in the sequence will be reanalyzed.

Continuing Calibration and Verification Standards

A C3 standard will be analyzed at least every 10 test samples and at the end of the analytical sequence. The concentration of the target analyte should be ± 25% of the theoretical concentration. If a check standard fails the ± 25% accuracy criterion, all samples between the previous successful laboratory check standard and the next successful laboratory check standard must be reanalyzed.

Sensitivity Check Standards

A sensitivity check standard at (i.e. C1 standard) will be analyzed near the end of the sequence. Monitored ions should be detected with ≥ 3:1 signal-to-noise ratio.

Test Sample Concentrations Outside Calibration Curve Range

If a target analyte is detected in a test sample and the concentration is below 0.5× C1 level, the concentration will be flagged as estimated. If a target analyte is detected and the concentration is at or above 0.5× C1 level, then the actual concentration will be reported.

If the concentration of a target analyte exceeds the upper calibration limit, the sample will be diluted and reanalyzed to bring the concentration within the calibration range.

Reporting

The analyst will assemble a data package containing the date of analysis, instrument identity, and quantitative results. Excel spreadsheets will be used to determine precision results. A brief report that discusses the analytical results and any anomalies will be provided.

Sample Disposal

Following analysis, data review, reporting, and acceptance of the analytical results, any remaining sample extracts from a given trial will be disposed of following established laboratory procedures.

Scope and Applicability

This protocol describes the general procedures implemented at Battelle Columbus for the determination of thiodiglycol (TDG), pinacolylmethylphosphonic acid (PMPA), and methylphosphonic acid (MPA) in aqueous solutions by Liquid Chromatography-Mass Spectrometry (LC-MS/MS). Isotopically labeled TDG, PMPA, and MPA are used as internal standards. The MPA methodology is yet to be developed; procedures herein may be modified prior to the start of test sample analysis.

Analytical Procedure

Reagent Preparation

Liquid Chromatography Mobile Phase

TDG Mobile Phase: Into a 500 mL volumetric flask place 50 mL of methanol, 1 mL of 1 M formic acid, and 1 mL of 1 M ammonium formate. Adjust to 500 mL final volume with Milli-Q water. Proportional volumes may be used as needed.

PMPA Mobile Phase: Into a 500 mL volumetric flask place 150 mL of acetonitrile and 0.5 mL of formic acid (approximately 99%). Adjust to 500 mL final volume with Milli-Q water. Proportional volumes may be used as needed.

MPA Mobile Phase: To be determined. May be binary gradient composition.

Standards and Test Sample Preparation

Intermediate and Calibration Standard Solutions

TDG Working Standard Solution (4000 ng/mL): Dilute 40 µL of TDG stock solution (Cerilliant, 1000 µg/mL solution in methanol) to 10 mL final volume with Milli-Q water. Store refrigerated up to 3 months.

PMPA Working Standard Solution (4000 ng/mL): Dilute 40 µL of PMPA stock solution (Cerilliant, 1000 µg/mL solution in methanol) to 10 mL final volume with Milli-Q water. Store refrigerated up to 3 months.

MPA Working Standard Solution (4000 ng/mL): Dilute 40 µL of MPA stock solution (Cerilliant, 1000 µg/mL solution in methanol) to 10 mL final volume with Milli-Q water. Store refrigerated up to 3 months.

Calibration Curve Standard Solutions: Prepare separate calibration curves as tabled below using Milli-Q water as diluent. Store refrigerated. TDG and PMPA solutions are stable up to 60 days; stability of MPA solutions is to be determined.

Table B-7. Calibration Curve Solutions

Cal Std ID	Volume of Working Standard Solution (µL)	Final Volume (mL)	TDG Conc (ng/mL)	PMPA Conc (ng/mL)	MPA Conc (ng/mL)
C1 (or IDL)	50	10	20	20	20
C2	100	10	40	40	40
C3	250	10	100	100	100
C4	500	10	200	200	200
C5	1000	10	400	400	400
C6	1500	10	600	600	600

Fortify 190 µL of calibration standard with 10 µL of appropriate WIS (see below), and vortex prior to analysis.

Internal Standards

TDG-$^{13}C_4$ Working Internal Standard (WIS): Dilute 200 µL of TDG-$^{13}C_4$ stock solution (Cerilliant, 100 µg/mL solution in methanol) to 10 mL final volume with Milli-Q water. Conc = 2000 ng/mL. Store refrigerated up to 3 months.

PMPA-$^{13}C_6$ Working Internal Standard (WIS): Dilute 200 µL of PMPA-$^{13}C_6$ stock solution (Cerilliant, 100 µg/mL solution in methanol) to 10 mL final volume with Milli-Q water. Conc = 2000 ng/mL. Store refrigerated up to 3 months.

MPA-^{13}C, D_3 Working Internal Standard (WIS): Dilute 200 µL of MPA-^{13}C, D_3 stock solution (Cerilliant, 100 µg/mL solution in methanol) to 10 mL final volume with Milli-Q water. Conc = 2000 ng/mL. Store refrigerated up to 3 months.

Test Samples

Each Field Spike, Field Blank, Post-extraction Spiked Field Blank, Method Blank, Method Spike, and 100% Recovery Standard test sample extract received with the analytical batch will be fortified with the appropriate IS. Add 10 µL of appropriate WIS to 190 µL of test sample. Vortex prior to analysis.

Instrument Operation

The spectrometer will be mass-calibrated, or have its calibration verified, prior to the start of analysis. The mass accuracy (residuals) after calibration must be ± 0.2 Da.
Two ion transitions (quantitation and qualifier ions) will be monitored for each target analyte. Peak areas will be determined. The ratio of the peak areas of the 2 transitions will be calculated.

Peaks must have signal-to-noise ratios $\geq$ 3:1 to be considered detected.

LC-MS/MS Operating conditions for TDG and PMPA are summarized in Table B-8.

Table B-8. Operating Conditions for TDG and PMPA

LC-MS/MS System	
HPLC Mass Spectrometer	Waters 2695 (or equivalent) Micromass Quattro II with Z-spray source (or equivalent)
Mass Spec Source	Electrospray, positive ion mode
HPLC Column	TDG: Restek Allure PFP propyl, 2.1 x 150 mm, 5 µm
	PMPA: Phenomenex Columbus C8, 2 x 50 mm, 5 µm
Column Temperature	Ambient
Mobile Phase (Isocratic)	TDG: 10% aqueous methanol containing 2 mM each of formic acid and ammonium formate
	PMPA: 30% aqueous acetonitrile containing 0.1% of formic acid
Flow Rate	0.3 mL/min (no split to MS)
Injection Volume	20 µL
Run Time	5 min for TDG and 2.5 min for PMPA
Retention times	Approximately 3.3 min for TDG and 1.3 min for PMPA
MRM Transitions	TDG: 123>105 and 123>87 TDG-$^{13}C_4$: 127>109 and 127>91
	PMPA: 181>97 and 181>79 PMPA-$^{13}C_6$: 187>79 and 187>97

MPA Operating Conditions

Infuse mass-labeled MPA (MPA-13C, D_3) solution into the spectrometer to collect precursor and product ions. Optimize cone and collision energy settings for found transitions.

Determine the linear calibration range of non-labeled MPA using a developed chromatographic method.

Check for the presence of non-labeled MPA in the MPA-13C, D_3 internal standard: chromatograph a solution of MPA-13C, D_3 that is prepared near the mid-point (or lower) of the non-labeled MPA linear calibration range. If the MPA-13C, D_3 is free of non-labeled MPA indications, the tested MPA-13C, D_3 may be tried as the concentration of internal standard for a calibration curve. If non-labeled MPA is found, analyze lower concentrations of MPA-13C, D_3 to find a concentration where the MPA level is below one-half of the lowest MPA calibration standard; the determined MPA-13C, D_3 concentration which is free of MPA indications may then be tried as the concentration of internal standard for a calibration curve.

The LC-MS/MS system used to analyze the test samples and associated controls for MPA will be the same as before (Waters 2695 or equivalent HPLC system coupled with a Micromass Quattro II or equivalent with Z-spray source mass spectrometer operated in the Electrospray positive ion mode). The MRM transitions for non-labeled MPA will be 97>79 and 97>47. The MRM transitions for MPA-^{13}C, D_3 and all other operating conditions (HPLC column, column temperature, mobile phase, flow rate, injection volume, run time, and retention times) are to be determined.

Quality Control

System Blanks

A system blank (Milli-Q water) will be analyzed at the beginning of the analysis to confirm system cleanliness.

A system blank will also be analyzed after the highest calibration standard; if carryover above 0.5 C1 exists, a second system blank will be analyzed before test samples run.

Blank + IS

The Blank + IS sample will be analyzed before the calibration curve to verify that the IS contributes less than 0.5 C1 of the target analyte's response.

Calibration curves

A set of calibration curve solutions will be analyzed at the start of each test sample batch. The calibration curve for each target analyte will be constructed by plotting the relative response of the quantitation ion of each analyte with respect to its internal standard (TDG relative to TDG-$^{13}C_4$; PMPA relative to PMPA-$^{13}C_6$; MPA relative to MPA-^{13}C, D_3) against the concentration of the target analyte. The recalculated concentrations of the standards used to generate each calibration curve should be within 15 percent of the theoretical value for that standard, except in the case of the lowest standard, which may be within 25 percent. The calibration curves should be linear, with coefficients of determination $\geq$ 0.99, with the origins excluded. One of the calibration points, other than the C1 standard, may be excluded if needed to meet these requirements.

Continuing Calibration and Verification (CCV) standards

A standard at C3 concentration will be analyzed at least every 10 test samples and at the end of the analytical sequence. The concentration of the target analyte should be ± 25% of the theoretical concentration. Both ion transitions should be detected.

If a CCV fails the ± 25% accuracy criterion, all samples between the previous successful laboratory check standard and the next successful laboratory check standard must be reanalyzed.

Sensitivity check standards

A sensitivity check standard at C1 will be analyzed near the end of the sequence. Both ion transitions should be detected with $\geq$ 3:1 signal-to-noise ratio.

Test Sample Concentrations Outside Calibration Curve Range

If a target analyte is detected in a test sample and the concentration is below 0.5× C1 level, the concentration will be flagged as estimated. If a target analyte is detected and the concentration is at or above 0.5× C1 level, then the actual concentration will be reported.

If the concentration of a target analyte in a test sample exceeds the upper calibration limit, the sample will be diluted and reanalyzed to bring the concentration within the calibration range.

Reporting

The analyst will assemble a data package containing the date of analysis, instrument identity, and quantitative results. Excel spreadsheets will be used to determine precision results. A brief report that discusses the analytical results and any anomalies will be provided.

Sample Disposal

Following analysis, data review, reporting, and acceptance of the analytical results, any remaining aqueous sample extracts from a given trial will be decontaminated with bleach.

Appendix C: Addendum

Testing and Quality Assurance Plan for the Evaluation of Wipe Sampling Methods for Collecting Chemical Warfare Agents (CWAs), CWA Degradation Products, and Toxic Industrial Chemicals from Various Surfaces

Addendum July 2, 2008

Approved by:

Stephen Billets 7-2-08

Stephen Billets — Date
U.S. EPA Task Order Project Officer

Appendix C: Addendum

Section B1, Experimental Plan of this document states: "Battelle will discuss the results of Phase I with the EPA TOPO and determine whether it is feasible to move forward to Phase II experiments as outlined in Figure 2. If the results from the Phase I experiments do not meet all the criteria as stated above, Battelle will consult with the EPA TOPO on revising the approach for the Phase II full-scale study accordingly."

Completion of Phase I experiments showed that the method for the laminate was reproducible (most RSDs < 20%; several < 10%); multi-analyte spiking was comparable to single-analyte spiking (most < 10% D); vertical wiping was comparable to horizontal wiping (most <10% D); and 48-hour holding of the wipes prior to extraction had a negligible effect on recovery (few percent lower recoveries from stored wipes versus freshly extracted wipes). However, only three of the 10 target compounds (VX, tetraethyl pyrophosphate, and pinacolylmethylphosphonic acid) had recoveries that met the primary data quality objective of greater than 70%. To address the findings, Phase II will be modified from what was originally planned by adding: a new wetting/extraction solvent, a new surface (vinyl tile), analysis by low resolution mass spectrometry, and two phosphonic acids. Two surfaces (carpet and bare wood) were removed due to their porosity. The project will continue to use the same pre-cleaned wipes, surface spiking procedure, wiping procedure, and quality control samples that were used in Phase I. This addendum describes the changes to the original plan that now will be incorporated into Phase II of the experimental design. These modifications are summarized in Tables 1, 2, and 3.

Target analytes: The original 10 target analytes included four CWAs (HD, HN-3, GD, and VX), four degradation products [1,4-dithiane, thiodiglycol (TDG), methylphosphonic acid (MPA), and pinacolylmethylphosphonic acid (PMPA)], and two organophosphorous pesticides [dichlorvos and tetraethyl pyrophosphate (TEPP)]. In Phase I, 1,4-dithiane, dichlorvos, and TEPP were measured by low resolution mass spectrometry-selected ion monitoring (LRMS-SIM) and the CWAs were measured by high resolution mass spectrometry-selected ion monitoring (HRMS-SIM). Both HRMS-SIM and LRMS-SIM analytical techniques will be evaluated in modified Phase II for all analytes. For efficiency, we will combine these seven analytes into one gas chromatograph (GC) analysis. Of the remaining three analytes, the phosphonic acids and TDG will continue to be analyzed by liquid chromatography-mass spectrometry (LC-MS-MS). In addition, we will add ethylmethylphosphonic acid (EMPA) and isopropylmethylphosphonic acid (IMPA) to the list of acid degradation products to be evaluated by LC-MS-MS in modified Phase II. The current LC-MS-MS acid method will be modified to add EMPA and IMPA. A commercially-available isotopically-labeled IMPA will be used as an internal standard for IMPA. There is no isotopically-labeled EMPA standard available, which requires that EMPA be quantified against the isotopically-labeled IMPA. In the absence of an isotopically-labeled EMPA to use as an internal standard, the quantitation of EMPA in this method may not be as accurate. The method, however, should still provide useful information on the sampling and analytical performance of this compound of interest.

Appendix C: Addendum

Concentration levels: The risk-based surface cleanup goals (Table 2) continue to be the driver. Consequently, HRMS-SIM must continue to be used to achieve these ultra-low levels. As shown in Tables 1 and 2, two concentration levels (1x and 10x of the risk-based surface cleanup levels) will be evaluated for the GC and LC analytes, respectively. An addition will be to evaluate and determine at what sensitivity level the LRMS-SIM could be utilized instead of HRMS-SIM since most typical analytical laboratories will not have HRMS-SIM capability. Table 3 summarizes the estimated detection limits of target analytes by GC-HRMS-SIM, GC-LRMS-SIM, and the proposed spiking levels. If detection for the seven GC analytes is achieved by LRMS-SIM from the 10x spiking level but not from the 1x spiking level, the detection capability of the LRMS-SIM for these target analytes will be extrapolated from the 10x spiking level.

Wetting solvent(s): Isopropyl alcohol (IPA) has been the only wetting solvent utilized to this point. In the modified Phase II, we will evaluate IPA and 1:1 acetone:dichloromethane (ACE:DCM) for the GC analytes and IPA and methanol for the LC analytes. The volume of wetting solvent for each wipe will continue to be 2 mL.

Wiping surfaces: Three of the five types of original test surfaces will be evaluated. Laminate, galvanized metal, and painted concrete will be tested. Bare wood and industrial carpet will be eliminated due to significant porosity and anticipated poor recoveries so that we can invest remaining resources into better understanding the performance of the method for other surfaces. We will add vinyl tile as a surface (Armstrong commercial flooring, Standard Excelon vinyl composition tiles, Pattern 51858, Imperial Texture, sandrift white, 1/8 inch thick). Coupons will continue to be prepared according to the procedure in Section B1.3 of the test/QA plan. We will also continue to evaluate smaller sized coupons (3.2 cm x 3.2 cm = 10 cm^2 surface) which can be wholly extracted by sonication for comparison of surface retention and wiping efficiency. Pre-treatment of the surfaces will involve pre-cleaning prior to use by wiping them with the pre-wetted cotton gauze wipes (with whatever wetting solvent is being used) and allowing the surface to air dry prior to spiking.

Surface spiking procedure: We will continue to use the same liquid spiking procedure as described in Section B1.5 of the test/QA plan. Briefly, all spiking procedures will be carried out in a fume hood. A group of four test coupons (triplicate test samples and one field blank) will be placed in a clean container inside the hood. An aliquot (1000 µL) of the spiking solution will be spiked onto each coupon at 5 spots, at a rate of 200 µL/spot. For each field blank, same amount of solvent (1000 µL) used for the preparation of the individual spiking solution will be spiked in the same manner as the field spike test coupons. After spiking, the coupons will be left in the hood for no more than five minutes for drying. The smaller sized coupons will be spiked in the same manner but the volume of the spike will be 0.1 mL of a 10-fold more concentrated spiking solution of GC target analytes. The GC and LC analytes will be in separate spiking mixtures.

Wipe sampling procedure: We will continue to use the same wiping procedure, as described in Section B1.6 of the test/QA plan. Briefly, the designated wiping area (10 cm by 10 cm) on the test coupon will be wiped with 2 pre-cleaned cotton gauze pads, each wetted with 2-mL of the wetting solvent (IPA, ACE:DCM, or methanol). The first wipe will be used to wipe the coupon area in a single direction from top to bottom, while the

second wetted wipe will be used to wipe the same coupon area in a single direction from left to right, with three strokes each. After the first stroke, the exposed surface of the first cotton gauze will be folded inward for the second stroke, and then folded again for the third stroke. The cotton gauze pad is folded again with the exposed surface inside; then placed in the original jar. The test coupon will then be wiped again with the second wipe using the same procedures as described above. The second wiped cotton gauze pad will be placed in the same container as the first wiped cotton gauze pad; then the container sealed with Teflon tape and refrigerated for 48 hours prior to extraction and analysis. The purpose of this 48 hour storage time is to simulate field sample handling and storage conditions of the wipe samples as well as the elapsed time between sampling and extraction. Wipe samples spiked with the target analytes, along with non-spiked wipes, will also be stored under the same conditions as the field samples. All spiked test coupons will be placed in the horizontal position for wiping.

Sample preparation: Preparation procedures for the GC and LC analyses are described in Section B1.7 of the test/QA plan. We will continue to use ACE:DCM by ASE as the extraction procedure for the GC analytes. Each smaller coupon will be sonicated with 3x10 mL of 1:1 acetone/DCM for 10 minutes each time then extracts combined and concentrated to a final volume of 1 mL. The LC analytes will be extracted with 10 mL of Milli-Q deionized water instead of 7 mL to improve the extraction efficiency of target analytes from the wipe matrix.

Sample analysis: All of the GC samples will be analyzed by HRMS-SIM and LRMS-SIM (following Appendix B of the test/QA plan). We will do some optimization of the GC-LRMS-SIM method to accommodate all seven GC analytes. All of the LC samples will be analyzed by LC-MS-MS following the protocol described in Appendix B of the test/QA plan. The LC-MS-MS protocol for the acid target analytes will be optimized to accommodate EMPA and IMPA in the same analysis.

QC samples: We will continue to use surface-coupon non-spikes, post-extraction spikes, spiked wipes, non-spiked wipes, and solvent spikes as QC controls for GC-MS-SIM (both HRMS and LRMS) and LC-MS-MS analyses.

Appendix C: Addendum

Table 1. Summary of Groups I and II GC-MS-SIM [a] - Modified Phase II Approach

Type of Surface	Multi-analyte Spike	Spiking Level 1 (10x) µg/ Sample [b]	Spiking Level 2 (1x) µg/ Sample [b]	Residential Risk Based Cleanup Goals µg/Sample	Number of Samples							
					Surface Coupon Spikes		Surface Coupon Non-Spikes		Post-extraction Spikes [g]	Spiked Wipes [d, h]	Non-Spiked Wipes [d, i]	Solvent Spike [j]
					Wipe [c, d, e]	Sonicate [d, e, f]	Wipe [c, d]	Sonicate [d, f]				
Laminate,	1,4-Dithiane	0.400	0.040	210	12	6	2	1	2	8	2	2
Galvanized Metal,	GD	0.080	0.008	0.086								
	HD	0.080	0.008	0.0081								
Painted Concrete,	HN-3	0.080	0.008	0.0081								
	VX	0.120	0.012	0.013								
and	Dichlorvos	0.400	0.040	0.220								
Vinyl Tile	TEPP	0.400	0.040	0.220								

[a] Samples in Table 1 will be generated for each of the four surfaces (laminate, galvanized metal, painted concrete, and vinyl tile) and analyzed by GC-LRMS-SIM and GC-HRMS-SIM with the exception of the spiked wipes, non-spiked wipes, and solvent spikes which are independent of the surface so they will only be generated for each batch.

[b] Spiking level is for the 10 cm x 10 cm coupons, the 3.2 cm x 3.2 cm coupons, and the spiked and stored wipes. The 10x is equivalent to 20x first calibration (C1) level.

[c] Two wipes will be used for each sample. One wipe will be used to wipe the coupon from top to bottom and the second one from left to right. Both wipes will be extracted/analyzed as a single sample. Half the wipes are wetted with 2 mL of IPA each and the other half are wetted with 1:1 ACE/DCM.

[d] Each extract will be concentrated to a final volume of 1 mL.

[e] Three replicates will be prepared at two spiking levels. For wipes, two wetting solvents (IPA and 1:1 ACE/DCM) will be evaluated.

[f] Each coupon is sonicated with 3x10 mL of 1:1 ACE/DCM for 10 min each time then extracts combined and concentrated to a final volume of 1 mL.

[g] Post-extraction spike is only conducted on one non-spiked sonicated surface extract of each surface at each spiking level

[h] Two replicates at each spiking level and each wetting solvent

[i] One non-spiked wipe for each wetting solvent evaluated.

[j] One solvent spike will be prepared at each spiking level in 100% acetone.

Appendix C: Addendum

Table 2. Summary of Group III LC-MS-MS - Modified Phase II Approach

Type of Surface [a]	Multi-analyte Spike	Spiking Level 1 (10x) µg/ Sample [b]	Spiking Level 2 (1x) µg/ Sample [c]	Residential Risk Based Cleanup Goals µg/Sample	Number of Samples							
					Surface Coupon Spikes		Surface Coupon Non-Spikes		Post-extraction Spikes [g]	Spiked Wipes [d, h]	Non-Spiked Wipes [d, i]	Solvent Spike [j]
					IPA-Wetted Wipe [d, e]	Methanol-Wetted Wipe [d, e, f]	IPA-Wetted Wipe [d]	Methanol-Wetted Wipe [d, f]				
Laminate, Galvanized Metal, Painted Concrete, and Vinyl Tile	MPA	4.0	0.40	520	6	6	1	1	4	8	2	4
	EMPA	4.0	0.40	NA								
	IMPA	4.0	0.40	2100								
	PMPA	4.0	0.40	NA								
	TDG	4.0	0.40	5400								

[a] Samples in Table 2 will be generated for each of the four surfaces (laminate, galvanized metal, painted concrete, and vinyl tile) and analyzed by LC-MS-MS with the exception of the spiked wipes, non-spiked wipes, and solvent spikes which are independent of the surface so they will only be generated for each batch.

[b] Since the final extract volume is 10 mL for Group III wipe samples, the theoretical concentration of target analytes is 0.4 µg/mL which is 20 x C1 cal level

[c] Since the final extract volume is 10 mL for Group III wipe samples, the theoretical concentration of target analytes is 0.04 µg/mL which is 2 x C1 cal level

[d] Two wipes will be used for each sample. For surfaces, one wipe will be used to wipe the coupon from top to bottom and the second one from left to right. Both wipes will be extracted together and analyzed as a single sample. A wipe is wetted with either 2 mL of IPA or 2mL of methanol.

[e] Three replicates will be prepared at each spiking level

[f] A different wetting solvent may be attempted instead, if another EPA NHSRC study suggests that methanol is not a good wetting solvent.

[g] Two post-extraction spikes will be conducted on each non-spiked surface extract, one at each spiking level

[h] Two replicates at each spiking level and for each wipe wetting solvent

[i] One replicate for each wipe wetting solvent

[j] Two solvent spikes will be prepared for each wetting solvent, one at each spiking level

NA = Cleanup goal is not available

Appendix C: Addendum

Table 3. Comparison of Estimated Instrument Detection Limits (IDL) for Target Analytes by GC-HRMS-SIM and GC-LRMS-SIM to Residential Risk Based Cleanup Goal and Proposed 10x and 1x Spiking Level

Target Analyte	Residential Risk Based Cleanup Goals ng/Sample	GC-HRMS-SIM Estimated IDL ng/Sample [a]	GC-LRMS-SIM Estimated IDL ng/Sample [a, b]	10x Spiking Level ng/Sample	1x Spiking Level ng/Sample
1,4-Dithiane	210,000	0.066	5.0	400	40
GD	86	0.030	10	80	8.0
HD	8.1	0.330	4.0	80	8.0
HN-3	8.1	0.006	20	80	8.0
VX	13	0.660	66	120	12
Dichlorvos	220	0.45	10	400	40
TEPP	220	1.1	10	400	40

[a] Detection limit for each analyte is based on a 3:1 S/N of the qualifier ion. Minimum of 2 ions per analyte are monitored by GC-HRMS and up to 3 ions by GC-LRMS.
Note that a sample is a 10 cm x 10 cm coupon that is wiped, or a 3.2 cm x 3.2 cm coupon that is sonicated.
[b] GC-LRMS-SIM IDLs are based on other Battelle projects.

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