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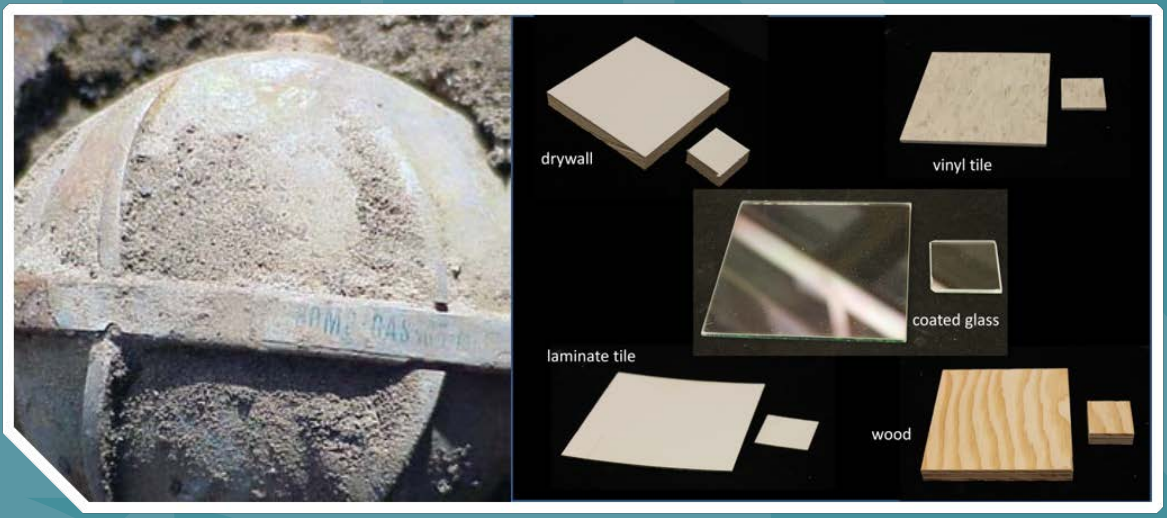
Evaluation of Chemical Warfare Agent Wipe Sampling Collection Efficiencies on Porous, Permeable, or Uneven Surfaces



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Evaluation of Chemical Warfare Agent Wipe Sampling Collection Efficiencies on Porous, Permeable, or Uneven Surfaces

Technical Report and Sampling, Extraction, and Analysis Procedure

United States Environmental Protection Agency

Cincinnati, OH 45268

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Executive Summary

Despite the fact that wipe sampling is commonly performed and the data produced by this technique is used to make numerous decisions, there is no strong consensus on the best method for collecting a wipe sample(s). It is generally agreed upon that in order to produce reproducible quantitative results, consistent wetting solvents, wipe materials, sampling techniques, and sampling areas must be used. Furthermore, proper wetting solvents should be selected with consideration of the analyte of interest. Conventional practices dictate that wet wipes are better than dry wipes for the collection of organic chemicals. This study was designed to understand factors affecting wipe sampling for specific chemical warfare agents (CWAs), including sarin (GB), soman (GD), cyclosarin (GF), sulfur mustard (HD), and *O*-ethyl-*S*-(2-diisopropylaminoethyl) methylphosphonothioate (VX) from non-ideal (e.g., porous and permeable) surfaces, including drywall, vinyl tile, laminate, coated glass, and wood. Pesticides, diazinon (DZN) and malathion (MA), were tested in addition to CWAs because literature data already exists and a comparison is possible between previous work and the experimental investigations described in this report.

The experimental strategy for this study is considered follow-on work stemming from previous collected data. The previous work identified Kendall-Curity® gauze as a preferred wipe when sampling for CWAs based on holding time stability studies and the absence/low levels of contaminants/interferences present in the wipe material. However, additional commercially available wipe materials will need to be tested. Therefore, a Dukal™ gauze wipe was tested to investigate potential contaminants that might interfere with CWA detection and a two-week long stability study was performed to determine the stability of CWA spiked onto the Dukal™ wipe when stored under refrigerated conditions (2-4 °C). Experiments were performed with coupon surface areas of either 10 cm^2 or 100 cm^2. The 10-cm^2 coupons were of a size that could easily be extracted in a 2-ounce jar (to provide comparative data for CWA recoveries generated by direct extraction) and the 100-cm^2 coupons better represented the area of a surface that might typically be sampled by wipe extraction. In addition, CWA, at a normalized surface concentration of 0.1 µg per cm^2 surface area, were spiked on coupons of the tested surfaces. Wipes were wetted with either dichloromethane (DCM) or isopropanol (IPA) before sampling for CWA. The effects of wipe type, coupon surface area, and solvent used to wet the wipe (i.e., wetting solvent) were tested. The utility of VX-d_{14} as an extracted internal standard was also tested.

Although different wipe wetting solvents were investigated, dichloromethane was used as the only extraction solvent for both the Kendall-Curity® and Dukal™ wipes. Both wipe materials were found to have similar alkane and phthalate contaminants, at fairly comparable concentrations. Thus, both the Kendall-Curity® and Dukal™ wipes were recommended to be cleaned prior to use, if possible, by solvent extraction. CWA spiked on the Dukal™ wipes, at tested concentrations of 0.1 µg and 1 µg, were stable on wipes stored under refrigeration, except for VX. The Dunnett's Test showed that VX concentrations measured at Day 14 were statistically significantly lower than those measured at Day 0 (e.g., only 53% of the VX spiked at 1 µg was recovered).

Recoveries for CWA and the pesticides from the surfaces of painted drywall, vinyl tile, laminate, coated glass, and wood were analyte-dependent, matrix-dependent, and highly variable, as might be expected when working with porous/permeable surfaces. Average recoveries (n = 3) of GB, GD, HD, GF, VX, diazinon, and malathion from large (100 cm^2 surface area, spiked with 10 µg each analyte) and small

(10 cm^2 surface area, spiked with 1 µg each analyte) coupons were determined under various extraction conditions. Wipe sampling experiments were performed with Kendall-Curity® and Dukal™ wipes using DCM or IPA as the wetting solvent. ANOVA was used to test for statistically significant differences in the average recoveries. The tables presented in the report contain recovery efficiencies for the target CWAs using both wipe types on each tested surface and direct extraction. Other factors that were tested in this investigation (e.g., wetting solvent) and statistical analyses for each surface type are presented. Based on the data within the tables, the findings are summarized below and should be viewed as general statements for porous/permeable surfaces as the trend may not apply to all tested analytes and/or matrices.

- Painted drywall matrix
  - In general, analyte recoveries by wipe sampling were < 50%
  - Coupon size may affect analyte recoveries (in general, use of the small coupon yielded greater analyte recoveries)

- Vinyl tile
  - Analyte recoveries were highly variable
  - Coupon size, wipe type, and wetting solvent may affect analyte recoveries
  - Wipe type, wetting solvent, and coupon size may affect analyte recovery

- Laminate
  - The more volatile CWAs (GB, GD, HD, and GF) were unable to be recovered from the surface
  - VX, malathion, and diazinon recoveries were typically > 30%
  - Coupon size, wipe type, and wetting solvent may not affect VX, malathion, and diazinon recoveries

- Coated glass
  - GB and GD were unable to be recovered from the surface
  - HD and GF recoveries ranged between non-detect (ND) to ~ 20%
  - VX, malathion, and diazinon recoveries were typically > 50%
  - Coupon size may affect GF, VX, malathion, and diazinon recoveries

- Wood
  - Recoveries of target analytes from wood were consistently lower than other matrices; GB, GD, HD, and GF were unable to be recovered by wipe sampling
  - VX was only detected on the small coupon when IPA was used as a wetting solvent
  - Malathion and diazinon were only detected when the Kendall-Curity® wipe was used to sample the small coupon and recoveries were < 45%
  - ANOVA tests could not be performed for any of the analytes due to the high number of non-detects (or the low number of detectable recoveries)

The following experiments performed in this study suggest that there was no clear "universal wetting solvent" when sampling the tested surfaces. Recoveries with the Kendall-Curity® wipes appeared to be higher than those observed with the Dukal™ wipes. Presumably, this was due to the larger size of the

Kendall-Curity® wipes (3” x 3”, versus the 2” x 2” size of the Dukal™ wipe) and the fact that the Kendall-Curity® wipe had the ability to hold more solvent (5 mL, versus the 1.5 mL held by the Dukal™ wipe). Further investigation is needed to compare wipes of similar size, ply, and wetting solvent volumes to confirm whether a specific wipe type is preferred or if material characteristics are a determining factor for analyte recoveries. Analyte recoveries could also be affected by coupon size. There are many factors (material type, wipe type, wetting solvent, wetting solvent volume, etc.) that can affect analyte recovery from porous/permeable surfaces and further investigation is needed to determine if surface area, or a combination of any of the factors listed above, play a significant role with respect to recovery efficiencies.

CWA and pesticide recoveries by direct extraction and by wipe sampling of the small coupons were compared using ANOVA. Direct extraction yielded statistically-significant, higher CWA recoveries than wipe sampling for the removal of GB from painted drywall, GD from vinyl tile, GF from painted drywall, HD from painted drywall and vinyl tile, VX, from vinyl tile and coated glass, malathion from painted drywall and vinyl tile, and diazinon from painted drywall and vinyl tile. Direct extraction results suggest that wipe sampling might underestimate CWA concentrations on/in these matrices. Wipe sampling most likely will only account for analyte on the surface and not necessarily from within a porous/permeable material. Thus, care must be taken when wipe sampling is performed and when interpreting results produced from wipe sampling. The resulting implication is that a “non-detect” produced by wipe sampling cannot be equated with the lack of CWA in a material.

Isotopically-labelled VX (VX- d_{14}) was used as an extracted internal standard to improve the accuracy of VX recovery from the tested surfaces. In almost all cases, measured VX recoveries considering VX- d_{14} responses were closer to expected recovery values (i.e., closer to 100 % recovery) than samples that did not use this extracted internal standard. The use of VX- d_{14} allowed for a more accurate estimation of VX concentrations when signals were low either due to background noise and/or matrix interferents. Data suggest that the use of labelled extracted internal standards for all contaminants of interest are desirable in future work when dealing with porous/permeable surfaces.

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Abbreviations/Acronyms

2-FB	2-fluorobiphenyl
ANOVA	Analysis of Variance (statistical analysis technique)
CCV	Continuing calibration verification
CWA	Chemical Warfare Agent
DCM	Dichloromethane
DZN	Diazinon
EPA	United States Environmental Protection Agency
GB	Sarin
GC	Gas Chromatograph
GC/MS	Gas Chromatography/Mass Spectrometry
GD	Soman
GF	Cyclosarin
HD	Sulfur mustard (distilled)
IPA	Isopropanol
IS	Internal Standard
KC	Kendall Curity® gauze wipe
LLNL	Lawrence Livermore National Laboratory
MA	malathion
MS	mass spectrometer
NB-d_5	Nitrobenzene-d_5
ND	non-detect
NIST	National Institute of Standards and Technology
NMR	Nuclear Magnetic Resonance Spectroscopy
OP	Organophosphorus pesticideoz Ounce
PFTBA	Perfluorotributylamine
P/N	part number
PTFE	polytetrafluoroethylene
ter-d_{14}	Terphenyl-d-$_{14}$
TIC	Total Ion Chromatogram
VOA	Volatile Organic Analysis
v/v	Volume/volume percent
VX	*O*-ethyl-*S*-(2-diisopropylaminoethyl) methylphosphonothioate
VX- d_{14}	Deuterated *O*-ethyl-*S*-(2-diisopropylaminoethyl) methylphosphonothioate

1.0 Introduction

Recovering from a chemical warfare agent (CWA) incident in an urban setting can present a myriad of challenges when characterizing the site and determining the extent of contamination. Contaminated areas within this setting can include materials of different morphologies and types, such as walls, floors, and furniture. Although direct extraction may be the preferred process, it is often not feasible when investigating these surfaces; thus, wipe sampling becomes the preferred technique. Direct extraction and wipe sampling each have advantages and disadvantages. Wipe sampling, as a collection technique, can be performed easily, rapidly, and without destruction of the tested surface; however, wipe sampling might not remove as much analyte from a material as direct extraction. For example, wipe sampling can only remove analyte from the surface of a material and not from within a material, which can be problematic when sampling porous surfaces. Direct extraction of a bulk material has the potential to remove analytes that have penetrated into a material, but may also extract numerous interferents from the material as well resulting in the potential for false positives or difficulty identifying target analytes. For this reason, it is important to understand analyte recovery efficiencies when interpreting wipe sampling and direct extraction data from bulk materials. Furthermore, it is important to understand the quantities of CWA that might still be present in a material after wipe sampling and direct extraction procedures are performed and the potential maximum recovery efficiencies from each technique.

Despite the fact that wipe sampling is commonly performed, and the data produced by this technique can be used to make numerous decisions, a recent review of wipe sampling (1) concluded that "there is not an overwhelming consensus on how to take a wipe sample for collecting CWAs, organophosphorus pesticides, and other toxic industrial chemicals from surfaces." In order to produce quantitative results, consistent wetting solvents, wipe materials, sampling techniques, and sampling areas must be used. Earlier work by the U.S. Environmental Protection Agency (EPA) found that "Experience and consistency of technique were determined to play significant roles concerning the overall accuracy and precision, in obtaining surface samples" (2). In addition, that same study concluded that: wetted wipes collected more analyte than dry wipes; wetting solvents should be selected with consideration of the analyte of interest; there was an apparent correlation between surface area of the wipe material and analyte recovery; and that analyte recoveries depended, in part, on the porosity of a surface.

This investigation was a follow-on project from a previous study that examined wipe sampling on non-porous surfaces contaminated with CWAs (3, 4). The interpretation of CWA wipe efficiency results was complicated because of the compounding effects of analyte volatilization and degradation. CWA wipe sampling from the previous investigation included a stainless steel and glass surface. Each surface was tested with several different wipe materials, including cotton gauzes (one from Kendall-Curity® and one from Certified Safety©), a glass fiber filter, and a cellulose fiber filter. The investigated wetting solvents included DCM, 50/50 (v/v)

acetone/DCM, hexane, and IPA. The previous study focused on wipe sampling of non-porous/impermeable surfaces, such as stainless steel and glass, because these surfaces are expected to provide optimum analyte recoveries, thus, a best case scenario for recovering the analyte from the surface. The current study, described herein, sought to expand the knowledge of CWA wipe sampling from surfaces that are more difficult to sample because they are porous and/or permeable. Findings from the previous work (3) influenced the direction of this investigation and were used to implement some of the experimental parameters listed below:

- Previous investigation concluded that the Kendall-Curity® gauze was a generally acceptable material, because of its ability to be effectively pre-cleaned, its structural integrity, and its ability to retain wetting solvent. Other commercially-available wipes still need to be tested to ensure proper optimal wipes are available in addition to the Kendall-Curity® gauze wipe. Therefore, another commercially-available gauze wipe (Dukal™) was tested.

- A clear "best solvent" for CWA sampling could not be identified from the previous work. From an operational perspective; however, IPA was favored because it was least prone to evaporation and not destructive to the tested surfaces. CWA analytes are stable in DCM solvent; thus, IPA and DCM, were selected as wetting solvents for the wipes. Both are expected to easily penetrate the surface of the tested materials.

- The previous study used small sampling surface area coupons of 10 cm^2. The current investigation used a larger surface area (100 cm^2), which is a better representation of a wipe sampling area used to collect analytes. For comparative purposes, coupons having both 10 cm^2 and 100 cm^2 surface areas were tested. Direct extraction was also used to compare wipe efficiency results.

- Diazinon and malathion were included to investigate the behavior of these pesticides as CWA surrogates. Literature data exists regarding the wipe sampling of these chemicals for comparative purposes and these analytes were included in the previous work.

The purpose of this study was to investigate recovery efficiencies from sampling of porous/permeable surfaces by direct extraction and wipe sampling techniques. Specific CWAs, including sarin (GB), soman (GD), cyclosarin (GF), sulfur mustard (HD), and *O*-ethyl-*S*-(2-diisopropylaminoethyl) methylphosphonothioate (VX), and the pesticides diazinon (DZN) and malathion (MA) were tested. The tested surfaces evaluated in this study (painted drywall, vinyl tile, laminate tile, coated glass, and wood) represent a wide range of materials (e.g., chemical composition and properties, surface characteristics) that are commonly found in many urban locations. Some of these materials might be expected to be left in place during a remediation

process. Two different coupon sizes were used during the investigation (10- cm^2 and 100- cm^2). The 10-cm^2 coupons represent a size that could easily be extracted in a 2-oz jar (to provide comparative data for CWA recovery efficiencies generated by direct extraction) and the 100-cm^2 coupons represent the area of a surface that might typically be sampled by wipe extraction. Tests were performed with 1 µg of each CWA per small sample coupon and 10 µg of each CWA per large sample coupon so that in each test, a consistent, normalized surface coverage of 0.1 µg/cm^2 of CWA was used. Specific combinations of wipes and wetting solvents were investigated to determine an optimal extraction of CWAs from the various surfaces. An analysis of variance (ANOVA) was performed to determine statistical differences in the measured recoveries. ANOVA provides a statistical test of whether or not the means of several groups are equal or a statistical significance exists between the measured groups.

To the extent possible, only questions involving analytical methods, and not those of environmental persistence of CWAs (i.e., the persistence of the CWAs on the surfaces), were examined. During the previous investigation, where CWAs were evaluated on surfaces (3), the study did not indicate a preferred wetting solvent, so both dichloromethane (DCM) and isopropanol (IPA) were evaluated. IPA was tested in addition to DCM because it was expected to be less destructive to surfaces than DCM.

The Kendall-Curity® gauze wipe (KC) was previously tested and determined to be the preferred wipe to use during CWA sampling activities (3); however, a similar wipe, Dukal™ gauze, was evaluated during this investigation for comparative purposes and to simulate the use of potentially multiple wipe types that might be used as part of the sampling process during an incident. The cleanliness of the Dukal™ wipe was assessed and compared to that of the Kendall-Curity® wipe. Additional testing of the Kendall-Curity® wipe was performed in parallel with tests of the Dukal™ wipe to ensure that both extraction and analysis processes for each wipe was performed under equivalent experimental conditions and that accurate comparisons between the two wipe materials were possible. The wipes tested “as is” (i.e., as received, directly from their packages) were extracted with DCM with the same procedure used to extract the wipe samples from surfaces (see Appendix A). The “pre-cleaned” wipes were cleaned by Soxhlet extraction with DCM for 10 cycles. GC/MS analyses were performed to determine the nature of contaminants that were present in the Dukal™ wipes and to determine if cleaning of these wipes was necessary prior to use for sample collection.

2.0 Study Objectives

Previously-tested wipe sampling methods (on metal and glass) were used to determine study objectives for CWA wipe collection efficiencies on the non-ideal (e.g., porous, permeable, or uneven) surfaces (3). Tested (non-ideal) surfaces included vinyl tile, wood, laminate, coated glass, and painted drywall. Objectives were designed to address the following questions listed below. Answers to these questions will help define the usefulness (and limitations) of wipe sampling versus direct sampling on non-ideal surfaces.

- Are there contaminants and/or interferents found within alternate wipe materials (e.g., Dukal™ wipes) that could potentially interfere with targeted CWA analysis?

- What is the stability of a CWA, spiked at 0.1 µg and 1.0 µg, on an alternate wipe material (e.g., Dukal™ wipe)?

- Do extraction efficiencies for Kendall-Curity® and Dukal™ gauze wipes differ when tested on non-ideal surfaces and is there a preferred wipe material for CWA sampling?

- Does a preferred wetting solvent exist for ideal or non-ideal surfaces (e.g., isopropanol or dichloromethane)?

- What is the effect (if any) from sampling a different surface area (e.g., 10-cm^2 coupon versus 100-cm^2 coupon of similar material) and will the result yield equivalent or different CWA recovery concentrations?

- Are collection efficiencies of wipe sampling and direct extraction techniques equivalent for coupons of the same surface area (e.g., 10 cm^2 surface area)?

- Does the use of a deuterated surrogate (e.g., VX-d_{14}) as an extracted internal standard (i.e., spiked prior to sample processing and analysis) provide better measurements for VX recovery concentrations and is this information applicable to other CWAs?

3.0 Experimental Conditions and Procedures

3.1 Materials

The following wipe materials were tested and are described below (Figure 1):

- Kendall-Curity® cotton gauze wipes, 3 in. x 3 in., sterile, cotton gauze (Kendall-Curity, 12-ply, P/N 1903, Tyco Heathcare Group LP, Mansfield, MA)

- Dukal™ gauze wipes, 2 in. x 2 in., sterile gauze (sold by Fisher Scientific, Pittsburg, PA, as North Co. by Honeywell, P/N 17986486; it should be noted that the wipe received was a gauze wipe, 12-ply, made by Dukal Corp. Ronkonkoma, NY)

Figure 1. Kendall-Curity® wipe (left) and Dukal™ wipe (right).

The following building materials were tested and are described below (Figure 2):

- **Painted drywall** – Standard, ½" drywall was obtained as surplus from onsite Lawrence Livermore National Laboratory (LLNL) facilities and are representative samples from commercial hardware stores. Two coats of combination paint and primer (Ultra-Pure White, Interior Matte, Behr Premium Plus Ultra, acrylic paint, P/N 175001, Behr Corp., Santa Ana, CA) were applied to the drywall.

- **Polymer-coated glass** – Glass coupons were cut from commercial window glass by Livermore Glass Company (Livermore, CA). Once cut, a coating (Prestige coating, P/N PR-70, run number 3024324013, 3M, St. Paul, MN) was applied per manufacturer's instructions (8). Dilute baby shampoo (Top Care by Topco Assoc. LLC, Skokie, IL), a couple of drops added to a liter of tap water, in a spray bottle, was used as a slip solution to position the coating. A squeegee tool was used to simultaneously adhere the coating to the glass, to remove all air bubbles, and to remove excess slip solution.

- **Wood** – Surplus plywood was obtained from onsite LLNL facilities and are representative samples from commercial hardware stores (top layer of solid wood is 3/32" thick).

- **Vinyl tile** – White vinyl tile materials (1/8" thickness) were purchased from commercial hardware stores and cut to appropriate size. (Excelon Sanddrift, P/N VCT 51858-45SF, Armstrong, Lancaster, PA).

- **Laminate** (laminate countertop) - The white 3' x 8' sheet, was obtained from commercial hardware stores and cut to appropriate size. (Designer White, P/N d354-60), Wilsonart LLC, Temple, TX).

All materials were cut to coupon sizes of approximately 10 cm^2 and 100 cm^2. The smaller coupon size was selected to allow the direct extraction of surface materials in 2-ounce (oz) jars. Furthermore, a direct comparison is possible between direct solvent extraction of a surface and wipe extraction of a coupon with the same surface area. The larger coupon size (100 cm^2) was selected to be comparable in size to a 10 cm x 10 cm surface area that might be sampled during an environmental remediation.

Solvents used for the wipe study included dichloromethane (DCM) (AMD Chromasolv®, >99.8% for gas chromatography (GC), P/N 34897-6X1L, Sigma-Aldrich, St. Louis, MO) and isopropanol (IPA) (anhydrous, 99.5%, P/N 278475-1L, Sigma-Aldrich, St. Louis, MO).

CWA analytes were synthesized at LLNL and spiked onto the various surfaces from a 10 µg/mL solution in DCM. They included sarin (GB), soman (GD), cyclosarin (GF), sulfur mustard (HD), and *O*-ethyl-*S*-(2-diisopropylaminoethyl) methylphosphonothioate (VX). Spiking solutions were made from neat agent in DCM. The purities of the neat agents were determined by nuclear magnetic resonance (NMR) spectroscopy to be 95%, 95%, 95%, 99%, and 96% for GB, GD, GF, HD, and VX, respectively. Malathion was obtained as a 100-µg/mL solution in cyclohexane (P/N 31558, Sigma Aldrich, St. Louis, MO). Diazinon, was obtained as a 100 µg/mL in acetonitrile (part number 45842, Sigma Aldrich, St. Louis, MO).

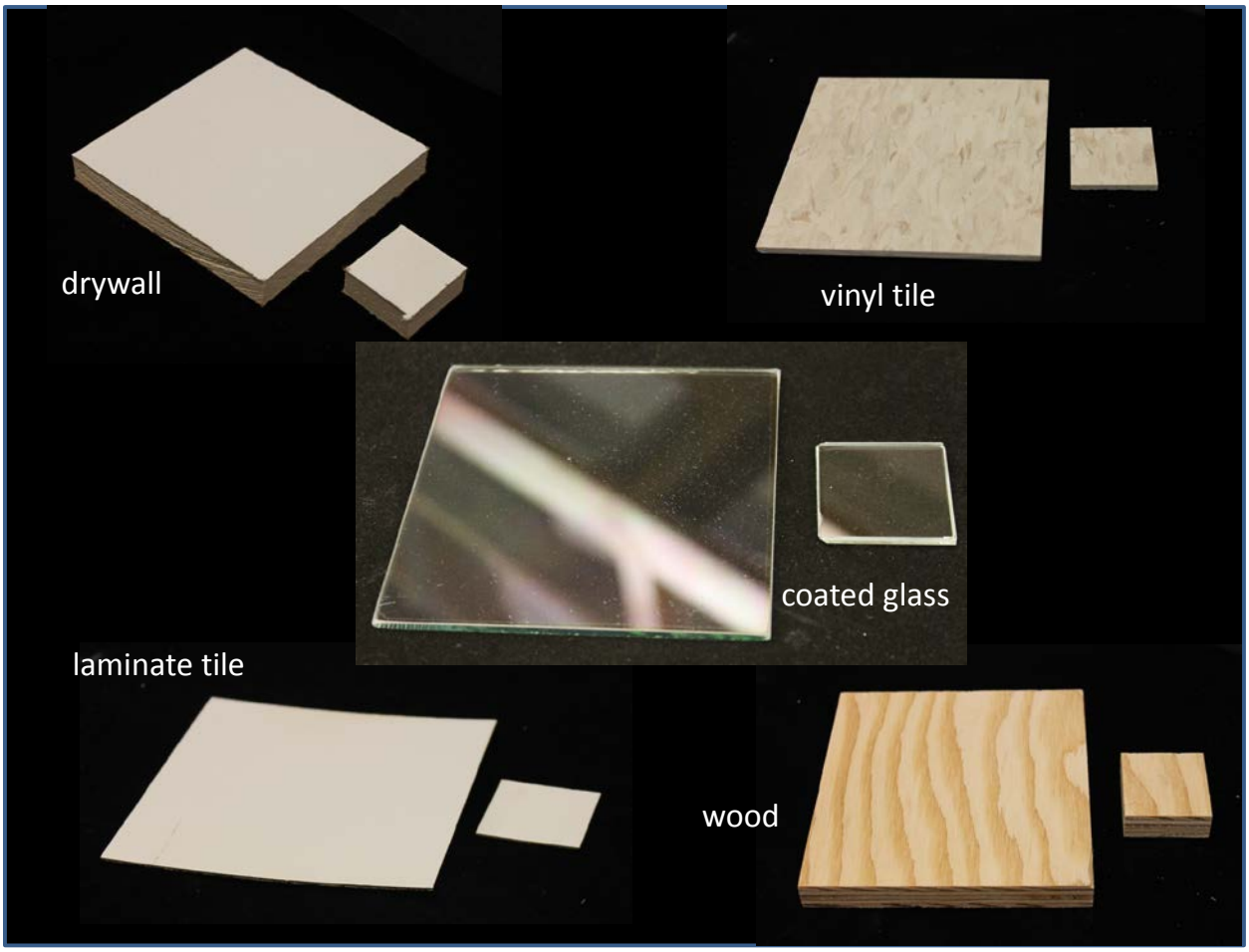

Figure 2. Materials tested in this study (100 cm^2 and 10 cm^2 coupons).

3.2 Extraction of Alternate Wipe Materials to Investigate Possible Interferences with Target CWAs

A single Dukal™ wipe was extracted with DCM, using the method described in Appendix A, §8, but without surrogate/internal standards. The resulting sample extract was reduced in volume to 1.0 mL and analyzed by gas chromatography/mass spectrometry (GC/MS) to investigate any potential contaminants or interferents that may be present in the native wipe materials prior to use with CWAs and target surfaces (Appendix A). Potential interferents were tentatively identified by comparison of their mass spectra to those contained in the NIST '08 Mass Spectral Database and discussed in Section 4.1. Duplicate samples were analyzed to determine if interferences were present in the Dukal™ wipe material.

3.3 Cleaning of Wipes

As suggested during the previous investigation (3), all wipes used for CWA analysis should be pre-cleaned prior to use to reduce any interference with CWA signal intensities and analytical capabilities. Because both wipes contained some interferents in the region where VX elutes (Table 1), all wipes used in this study were cleaned by Soxhlet extraction (10 cycles) with DCM as prescribed. Further details are discussed in Section 4.1.

3.4 Spiking of Coupons and Wipes

Coupons were spiked with CWAs, malathion, and diazinon from a multi-component, dilute solution (10 µg/mL each component) in DCM (see Appendix A, §8, for details of spiking procedure). The spiking solution standard was used within a day of preparation. Appropriate volumes of the solution were deposited on the matrices of interest using calibrated pipettes (Appendix A, §8). All 10-cm^2 coupons were spiked with 1 µg of each CWA and pesticide (spiked with 100 µL solution, deposited as five, 20-µL drops, of the 10 ng/µL stock solution). All 100-cm^2 coupons were spiked with 10 µg of each CWA and pesticide (spiked with 1000 µL solution, deposited as fifty, 20-µL drops, of the 10 ng/µL stock solution). Both sizes of coupons were spiked with the same normalized concentration of CWA (i.e., both size coupons were spiked with 0.1 µg CWA per square centimeter of surface area). The coupons were directly extracted or wiped as soon as solvent evaporation was complete (~ 5 minutes) to minimize the possibility of CWA loss due to evaporation or surface reactions as DCM will degrade surfaces (e.g., plastics).

3.5 Wipe Sampling Procedure for Tested Surfaces

A consistent, predetermined volume of solvent (Appendix A, 8.3) was used to wet each wipe material so that the wipe was saturated, 5.0 mL for the Kendall Curity® gauze wipes and 1.5 mL for the Dukal™ gauze wipes. Surfaces were sampled by first using a horizontal "Z" shaped pattern to wipe the entire surface of the coupon; then the wipe was folded inward so that the used portion is concealed. Once folded inward, the newly exposed part of the same wipe was used to sample the same surface in a vertical "Z" pattern. The coupons were held stationary during the wiping operation with solvent-rinsed forceps. The wipe or coupon was immediately placed in a

40-mL volatile organic analysis (VOA) vial and extracted with the appropriate amount of DCM solvent volume (Section 3.6 and Appendix A, §8) to determine CWA removal from the surface.

3.6 Extraction of Wipe Materials for the Detection of CWAs

The extraction process is summarized below and described in detail in Appendix A. After surface wiping was completed, the gauze wipe (or smaller coupon used for direct extraction) was placed in a pre-cleaned, 40-mL, clear, glass vial with polytetrafluoroethylene (PTFE)-lined screw cap. Surrogate solutions were added, in appropriate amounts (1 µg each compound), directly onto the wipe samples. All samples were extracted, twice, for 15 minutes each with 15 mL of DCM, using a shaker table. Prior to analysis, the combined sample extracts were evaporated using a gentle stream of clean, dry nitrogen (RapidVap unit and a Pierce Reacti-Therm™ III, with an evaporation module) to just below 1 mL. The sample extract was adjusted to a final volume of 1.0 mL with DCM and the appropriate amount of internal standard (to provide a concentration of 1.0 µg/mL for each internal standard compound – see Appendix A) was added prior to analysis.

Quality assurance and control samples and method blanks were included during the wipe extraction process. All quality assurance and control samples are presented in Appendix A. Method blanks did not contain CWA, but were extracted and treated in an identical manner to wipes used to sample CWA. Control samples consisted of 1 µg each CWA and pesticide, 1 µg each surrogate (see Appendix A, §7.0), and 1 µg each internal standard (see Appendix A, §7.0) spiked directly into 1.00 mL DCM.

3.7 Analysis of Wipe Extracts

Analysis conditions are briefly summarized below, but are described in greater detail in Appendix A, §10. The GC/MS analyses were performed with an Agilent 5975C MS coupled with an Agilent 7890 GC (both from Agilent Technologies, Inc., Santa Clara, CA). The GC/MS was tuned and calibrated, as needed, with perfluorotributylamine (PFTBA), using the vendor's algorithms and specifications. Prior to analysis of samples, a calibration curve in DCM was analyzed, followed by the analysis of a CWA test mixture, equivalent to the continuing calibration verification (CCV) standard, to establish that the GC/MS was functioning properly. Each batch of samples was analyzed with a corresponding method blank and control samples (Section3.6 and Appendix A). During the course of analysis, CCV standards, at 1 ng/µL, were analyzed for each analysis batch, which consisted of no more than twenty samples (Appendix A). The responses of these standards must be within 20% of the response of the initial calibration in order for the collected data between CCV checks to be considered valid. For GC/MS analyses, the surrogate and internal standards were consistent with those of EPA Method 8270 (4).

3.8 Holding Time Studies

A holding time study was previously performed by spiking CWAs on the Kendall-Curity® wipe (3). For comparison, experiments were conducted to determine the stability of CWAs spiked on DCM-wetted (0.5 mL) Dukal™ wipes, at amounts of 1 µg and 0.1 µg. CWAs were spiked on

the wetted wipes, stored in closed VOA vials in a refrigerator (2-4 ºC), and analyzed on Days 0, 2, 7, and 14to determine the stability of the analytes.

3.9 Statistical Analyses

A program called "R" (5) was used to perform statistical analyses to determine whether differences in measured CWA concentrations were statistically significant. Three statistical parameters were examined. The Dunnett's method was used in analysis of variance (ANOVA) to create confidence intervals for differences between the mean of each factor level and the mean of a control group. The Dunnett's Test was used to determine if there was a statistically significant decrease in CWA concentrations at various time points sampled during the holding time study. Secondly, a three-way ANOVA was used to determine if wipe type, solvent type, and coupon size significantly affected the concentrations of measured CWA. Finally, ANOVA was also used to test if concentrations measured by direct extraction of the small coupons were statistically different than those measured using wipe extraction of the small coupons.

4.0 Results and Discussion

4.1 Evaluation of Dukal™ Wipe Contaminants

The cleanliness of the Dukal™ wipe was assessed and compared to that of the previously-investigated Kendall-Curity® wipe (3). Figure 3 represents the total ion chromatograms (TICs) produced by analyzing the wipe extracts from both the Dukal™ and Kendall-Curity® wipes; the tentative identities (i.e., determined by match with the NIST mass spectral library) of the numbered peaks are presented in Table 1. Table 1 also contains the "reverse fit" value, which indicates how well the recorded mass spectrum agreed with its best match in the NIST database (with a value of 1000 being a perfect fit). The "reverse fit" value is generated by comparing the spectrum of the unknown and the library spectrum and ignoring any peaks in the unknown that are not in the library spectrum. Both wipes contained similar alkane and phthalate contaminants.

Figures 4 and 5 indicate a reduction of contaminants for both the Kendall-Curity® and for the Dukal™ wipes in the TIC region, the region in which VX, diazinon, and malathion elute, after cleaning. For comparative purposes, under the GC/MS conditions described in Appendix A, GB, GD, HD, GF, VX, diazinon, and malathion elute at retention times of approximately 6, 11, 13, 14, 22, 23, and 25 minutes, respectively. Thus, the TIC data suggest that both the Dukal™ and the Kendall Curity® wipes should be cleaned, if possible, before use. This conclusion is in agreement with that of the previous study, which also recommended that the Kendall-Curity® wipe be cleaned before use (3). In the previous study, CWA recoveries for pre-cleaned and "used as received" Kendall-Curity® gauze wipes were the same, with the exception that both VX and malathion showed statistically significant higher recoveries from uncleaned gauze than from pre-cleaned gauze. This, in part, was attributed to co-eluting interferences in the region of approximately 20–25 minutes in the TIC.

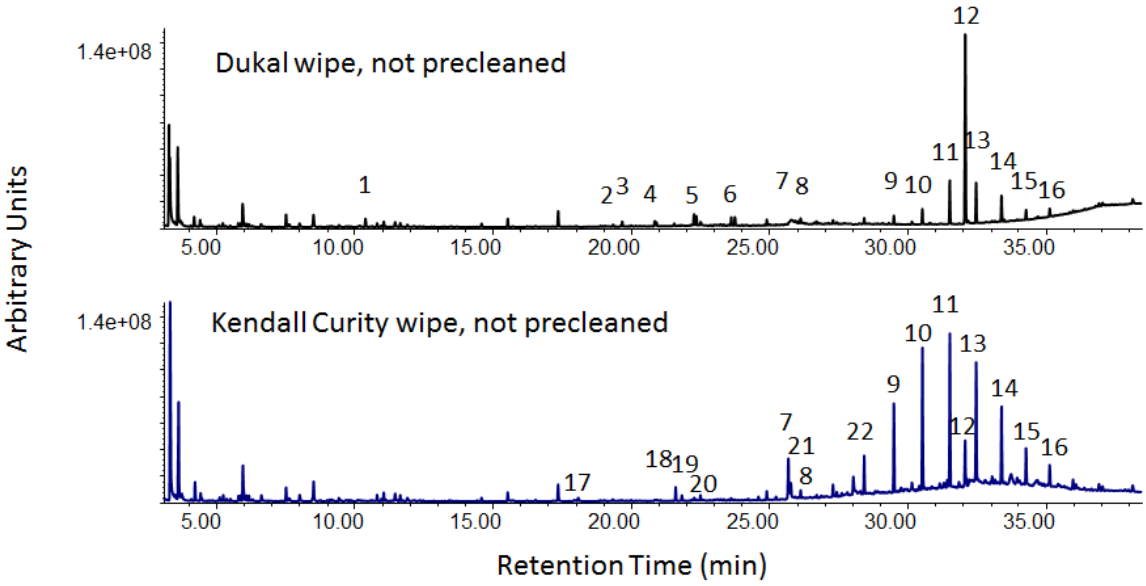

Figure 3. TICs for wipes that were received, extracted, and analyzed by GC/MS. Compounds were tentatively identified by library search and summarized in Table 1.

Table 1. Wipe Contaminants Tentatively Identified by GC/MS; Peaks Numbers Correspond to Those Listed in Figure 3

Peak	Tentative Identification	Retention Time (min)	Reverse Fit
1	2-(2-ethyoxyethyoxy)ethanol	10.39	967
2	2,4-di-tert-butylphenol	19.62	884
3	butylated hydroxytoluene	19.68	920
4	n-hexadecane	20.85	962
5	n-heptadecane	22.28	924
6	n-octadecane	23.63	943
7	n-hexadecanoic acid	25.73	930
8	n-eicosane	26.13	920
9	n-tricosane	29.50	909
10	n-tetracosane	30.53	959
11	n-pentacosane	31.54	907
12	di-n-octyl phthalate	32.09	856
13	n-hexacosane	32.50	909
14	n-heptacosane	33.41	890
15	n-octacosane	34.30	916
16	n-nonacosane	35.16	887
17	Surfynol 104	18.08	876
18	tributylphosphate	21.61	959
19	Uniplex 108	21.84	869
20	pentadecanal	22.51	915
21	dibutylphthalate	25.78	953
22	docosane	28.43	946

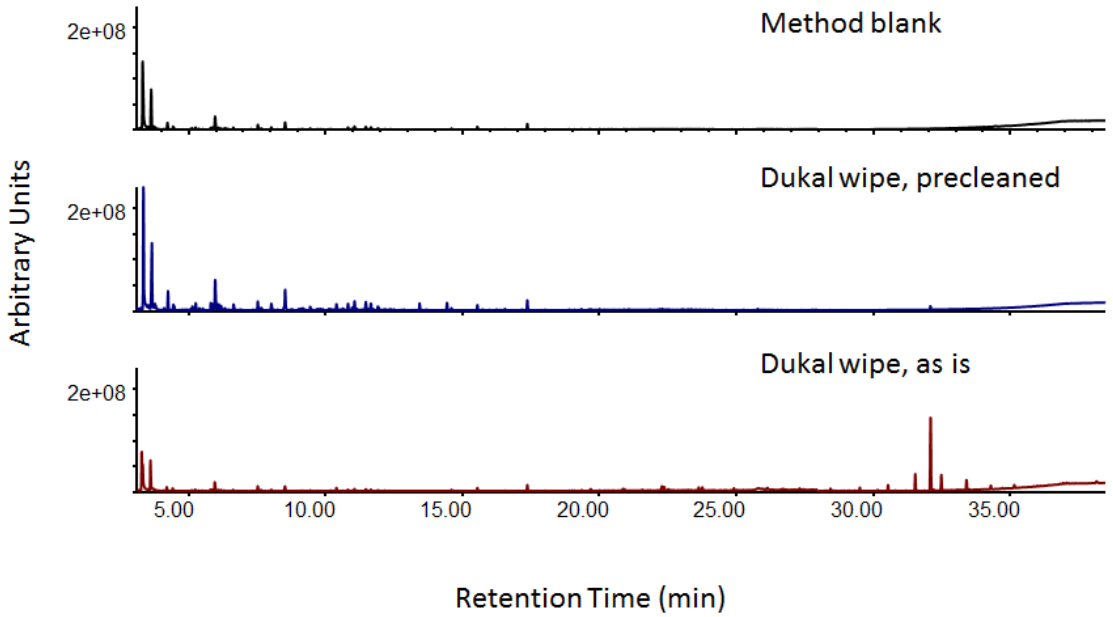

Figure 4. TICs for method blank and Dukal wipes pre-cleaned and "as received"

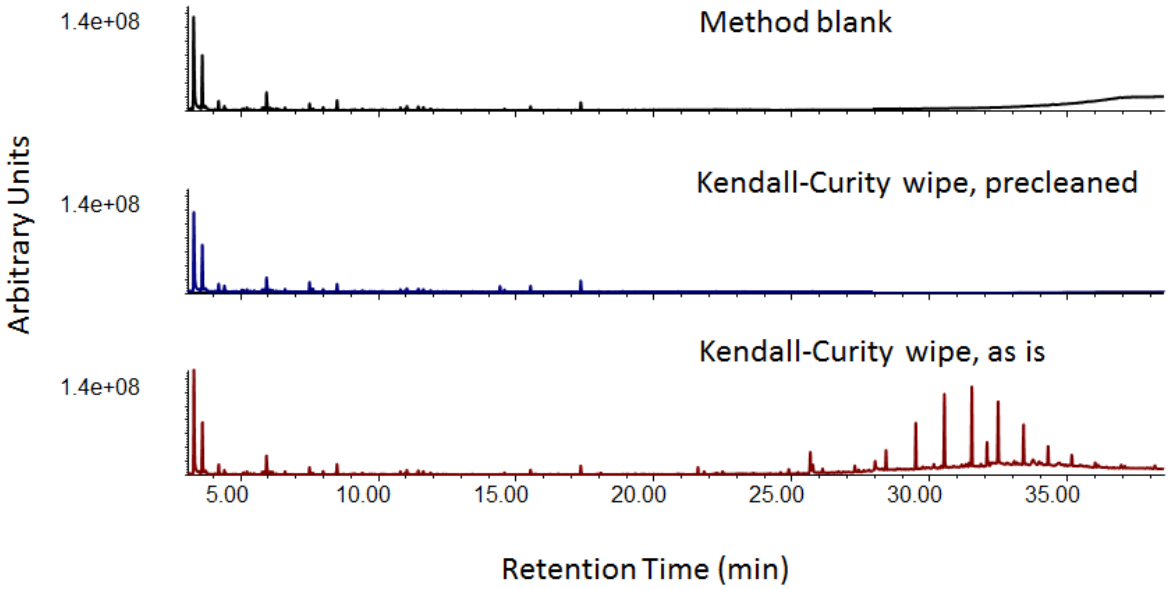

Figure 5. TICs for method blank and Kendall-Curity wipes pre-cleaned and "as received"

4.2 Surface Sampling using Different Wipes and Wetting Solvents

CWAs were spiked onto various surfaces and their average (n = 3) recoveries were determined for different wipes (Kendall-Curity® or Dukal™) and wetting solvents (IPA or DCM). Wipe sampling of both small (10 cm^2) and large (100 cm^2) coupons was conducted for each of the test materials. CWA and pesticide recoveries are organized by surface type and presented in Tables 2, 4, 6, 8, and 10. Comparison of CWA and pesticide recoveries obtained by direct extraction of the small coupons and by wipe sampling will be discussed in Section 4.3. Wipe recoveries are based on the analyte responses generated from calibration curve, unless noted.

Analysis of variance (ANOVA) was performed to determine statistical differences in the measured recoveries. Non-detections were replaced with random values generated from the uniform distribution ranging from zero to the detection limit when performing the statistical analyses. Generated substitute values averaged one-half the detection limit when using this approach. Overall, the values provided similar results to the existing method for substituting a fixed, one-half the detection limit. While the substitution of one-half the detection limit for non-detects is commonly used, the use of random values ranging from zero to the detection limit was the selected strategy because, with the use of substitute values that are the same, measurement variability is under-estimated. Using random values in the range from zero to the detection limit more closely represents the true, but unknown, variability in the data. More sophisticated methods (6) are not readily available for multi-factor analysis of variance and could not be used. In addition, nine or more detections within any group were required before performing statistical analyses. Most groups had 17 or more detections out of 24 results. Results of statistical analyses are presented in Tables 3, 5, 7, and 9.

Painted Drywall. CWA and pesticide recoveries from drywall were highly variable and analyte dependent, ranging from non-detect (ND) (for GB, sampled from a small coupon, using a Kendall-Curity® wipe, wetted with IPA) to 127 % (for malathion, extracted directly from a small coupon) (Table 2). Direct extraction of painted drywall yielded recoveries for the target analytes ranging from ~ 60 % (for GB) to > 80 % (for the other target analytes). Wipe sampling recoveries for the target analytes were 62 % or less.

Table 2. Average[a] Recoveries (%) for CWA, Pesticides, and Surrogates from Painted Drywall

Analyte	Direct extraction small	KC DCM small	KC IPA small	KC DCM large	KC IPA large	Dukal DCM small	Dukal IPA small	Dukal DCM large	Dukal IPA large
GB	57 ± 6	15 ± 12	ND	10 ± 3	6 ± 1 [b]	8 ± 4 [b]	4 ± 4 [b]	ND	10 ± 0
GD	114 ± 19	30 ± 26	24 ± 6	11 ± 3	13 ± 4	18 ± 4	15 ± 1	ND	11 ± 1
HD	82 ± 14	13 ± 7	11 ± 3	10 ± 2	8 ± 1 [b]	8 ± 3 [b]	9 ± 1 [b]	ND	8 ± 0 [b]
GF	115 ± 20	40 ± 20	24 ± 4	5 ± 3 [b]	19 ± 3	27 ± 7	21 ± 1	ND	5 ± 0 [b]
VX	94 ± 20	62 ± 17	41 ± 7	8 ± 1 [b]	27 ± 3	48 ± 29	45 ± 4	ND	11 ± 3
MA	127 ± 9	55 ± 13	17 ± 16	4 ± 1 [b]	9 ± 7 [b]	41 ± 7	17 ± 2	ND	ND
DZN	84 ± 12	41 ± 19	18 ± 5	6 ± 1 [b]	12 ± 3	29 ± 11	18 ± 2	ND	ND
NB-d_5	75 ± 10	57 ± 8	63 ± 5	71 ± 7	ND	74 ± 9	39 ± 3	81 ± 16	89 ± 7
2-FB	69 ± 4	56 ± 9	79 ± 5	78 ± 8	140 ± 0	70 ± 9	83 ± 2	74 ± 5	91 ± 7
PCP-d_5	84 ± 9	88 ± 9	86 ± 10	71 ± 6	140 ± 1	113 ± 8	101 ± 1	67 ± 7	90 ± 7
ter-d_{14}	74 ± 6	59 ± 7	84 ± 7	77 ± 5	150 ± 0	73 ± 11	87 ± 3	72 ± 6	90 ± 6

small = 10 cm^2 coupon spiked with 1 µg analyte; large = 100 cm^2 coupon spiked with 10 µg analyte

Abbreviations: 2-FB = 2-fluorobiphenyl, DCM = dichloromethane, DZN = diazinon, IPA = isopropanol, KC = Kendall-Curity wipe, MA = malathion, NB-d_5 = deuterated nitrobenzene, ND = non-detect, PCP- d_5 = deuterated phencyclidine, ter-d_{14}= deuterated terphenyl

Note: [a] average of three replicates ± the standard deviation of the measurements; [b] estimated average concentration was below lowest calibration level

Table 3. Statistical Analyses (ANOVA p-values [a]) of CWA and Pesticide Recoveries (Table 2) from Drywall

Tested Variable(s)	ANOVA p-values [a]						
	GB	**GD**	**HD**	**GF**	**VX**	**MA**	**DZN**
Wipe	0.48	0.10	0.54	0.025	0.19	0.16	0.16
Wetting Solvent	0.21	0.96	0.99	0.63	0.98	**0.0008**	0.087
Coupon Size	0.54	**0.010**	0.11	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
Wipe + Wetting Solvent	0.030	0.70	0.30	0.91	0.84	0.56	0.41
Wipe + Coupon Size	0.62	0.41	0.66	0.78	0.75	0.31	0.95
Wetting Solvent + Coupon Size	0.20	0.31	0.80	0.021	0.32	**<0.0001**	**0.0033**
Wipe + Wetting Solvent + Coupon Size	0.96	0.98	0.96	0.057	0.12	0.27	0.29

Note: [a] $p < 0.01$ indicates statistical significance; statistically significant values are highlighted and in bold font.

ANOVA analyses suggests that coupon size may be an important variable contributing to statistically-significant differences in recoveries (Table 3). CWA and pesticide recoveries on small coupons tended to be higher when compared to the larger coupon size for all tested solvents, although the error associated with the smaller coupons is also larger in some cases, which may be attributed to the solvent/matrix interactions. The increased ratio of solvent to surface area and the amount of time the target analytes are exposed to the surface (e.g., drying times on small vs large coupons) might play a role in higher recoveries for the smaller coupon size. Evaporation of solvent will most likely be facilitated when the solvent is distributed over a larger surface area. Further investigation is needed to determine the effect of coupon size and solvent for CWA recovery efficiencies from these surfaces.

Wetting solvent appeared to be a significant variable for the recovery of malathion as recoveries using DCM solvent were higher than for IPA. Interactions that occur between solvent and surface are difficult to determine. Although it is anticipated that DCM would be able to penetrate the surface of painted drywall to a greater extent than IPA, matrix interferences may also be greater due to the ability of DCM to compromise the surface and can be verified by examining matrix blanks. The data suggests that malathion may partition better into DCM than IPA, but may also be subjected to greater interferences associated with the painted drywall surface and use of DCM solvent. ANOVA tests also suggest a significant correlation of wetting solvent and coupon size for malathion and diazinon. From a statistical point of view, there was no clear best combination of wipe and wetting solvent to remove CWA and pesticides studied from the painted drywall surface.

Vinyl Tile. Recoveries for target CWAs and pesticides on vinyl tile were highly variable and analyte dependent (Table 4). For this matrix, volatile CWAs (GB, GD, HD, and GF) were not recovered from the large coupons when the Kendall-Curity® wipe was used with IPA wetting solvent or when the Dukal™ wipe was used with either IPA or DCM as a wetting solvent. The Dukal™ wipe holds less solvent (approximately two times less) than the Kendall-Curity® wipe, which can be attributed to smaller size or the how the material is woven because both wipes are of the same weight (12-ply). The inability of the Dukal™ wipe to hold a greater volume of solvent, may explain, in part, the observed non-detects. The ability of CWAs to easily penetrate into the vinyl tile might also contribute to low or no recoveries by wipe sampling. It is important to note that VX recoveries from direct extraction of the small coupons resulted in non-detection of the CWA, which is unexpected. VX is considered less-volatile than any of the tested CWAs and should result in a recovery result from the direct extraction process, especially since wiping results produced recoveries. As stated above, results from the vinyl tile surface were highly variable, which is likely attributed to the matrix interferences produced from the surface. The direct extraction process will result in greater matrix effects, and larger quantities of interferents, than surface wiping because the extraction solvent is directly interacting with the matrix for an extended time period versus surface wiping. Matrix interferences most likely resulted in the inability to reliably recover VX from the surface. More investigation is warranted.

ANOVA analyses suggest that statistically significant differences in recoveries were identified for most of the tested analytes, the type of wipe, wetting solvent, and coupon size (Table 5). For the vinyl tile, in general, the Kendall-Curity® wipe with DCM wetting solvent (on a small coupon) resulted in the highest recoveries. Statistically significant interactions between wipe and wetting solvent and wetting solvent and coupon size were observed.

Laminate. CWAs and pesticides were not recovered for many of the experiments using the laminate surface (Table 6). Laminate is not a rough surface and is not considered as porous as vinyl tile, suggesting the lack of recoveries for GB, GD, HD, and GF might be due to volatilization. Surrogate recoveries for nitrobenzene-d_5- and 2-fluorobiphneyl, which are considered to be volatile chemicals, were poor when spiked directly on the laminate surface for the direct extraction experiments. Surrogate recoveries for these two analytes were much higher when they were spiked directly on the wipes, suggesting that analyte volatility may play an important factor in analyte recovery from the laminate surface. Concentration effects were outside the scope of this study, but may help when attempting to understand and address volatilization and/or permeation of chemicals on a surface. Because the contact time with the surface was short and low concentrations of CWAs were used to spike the surface, the data suggests that CWAs at low concentrations are not well-recovered from laminate, most likely due to volatilization. Thus, natural attenuation might be a feasible decontamination approach in a remediation scenario for non-porous surfaces and areas where low CWA concentrations are known.

ANOVA analyses could not be performed for CWA analytes GB, GD, HD and GF due to the fact that too few detections were observed. ANOVA analyses for VX, malathion, and diazinon did not show any statistically significant differences in recoveries recorded using different wipes, wetting solvents, or coupon sizes (Table 7).

Table 4. Average[a] Recoveries (%) for CWA, Pesticides, and Surrogates from Vinyl Tile

Analyte	Direct extraction small	KC DCM small	KC IPA small	KC DCM large	KC IPA large	Dukal DCM small	Dukal IPA small	Dukal DCM large	Dukal IPA large
GB	59 ± 2	29 ± 5	ND	9 ± 1 [b]	ND	19 ± 1	ND	ND	ND
GD	107 ± 6	72 ± 2	ND	11 ± 3	ND	60 ± 4	7 ± 0 [b]	ND	ND
HD	84 ± 3	43 ± 1	ND	10 ± 3	ND	29 ± 3	ND	ND	ND
GF	114 ± 5	96 ± 2	16 ± 3	20 ± 7	ND	81 ± 4	12 ± 1	ND	ND
VX	ND	125 ± 3	72 ± 6	19 ± 11	27 ± 7	134 ± 1	62 ± 11	14 ± 2	15 ± 4
MA	138 ± 6	104 ± 3	35 ± 2	6 ± 3 [b]	ND	92 ± 2	34 ± 1	ND	ND
DZN	111 ± 5	84 ± 5	23 ± 2	13 ± 6	ND	86 ± 1	22 ± 1	ND	ND
NB-d_5	78 ± 6	56 ± 2	73 ± 9	74 ± 6	76 ± 6	88 ± 11	44 ± 4	117 ± 8	91 ± 2
2-FB	65 ± 4	44 ± 2	87 ± 4	78 ± 5	141 ± 1	78 ± 8	92 ± 10	119 ± 4	88 ± 2
PCP- d_5	41 ± 4	75 ± 2	99 ± 3	76 ± 6	125 ± 1	86 ± 5	109 ± 0	106 ± 3	100 ± 6
ter-d_{14}	53 ± 3	51 ± 3	100 ± 4	81 ± 7	151 ± 1	88 ± 7	95 ±10	131 ± 4	104 ± 6

small = 10 cm^2 coupon spiked with 1 µg analyte; large = 100 cm^2 coupon spiked with 10 µg analyte

Abbreviations: 2-FB = 2-fluorobiphenyl, DCM = dichloromethane, DZN = diazinon, IPA = isopropanol, KC = Kendall-Curity wipe, MA = malathion, NB-d_5 = deuterated nitrobenzene, ND = non-detect, PCP- d_5 = deuterated phencyclidine, ter-d_{14}= deuterated terphenyl

Note: [a] average of three replicates ± the standard deviation of the measurements; [b] estimated average concentration was below lowest calibration level

Table 5. Statistical Analyses (ANOVA p-values [a]) of CWA and Pesticide Recoveries (Table 4) from Vinyl Tile

Tested Variable(s)	ANOVA p-values [a]						
	GB	**GD**	**HD**	**GF**	**VX**	**MA**	**DZN**
Wipe	**0.0026**	**0.0088**	**0.0082**	**0.0002**	0.021	0.033	**0.0003**
Wetting Solvent	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
Coupon Size	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
Wipe + Wetting Solvent	**<0.0001**	**0.0031**	**0.0002**	**0.0003**	**0.0043**	0.97	**0.0024**
Wipe + Coupon Size	**<0.0001**	0.40	0.52	0.11	0.034	0.061	**<0.0001**
Wetting Solvent + Coupon Size	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
Wipe + Wetting Solvent + Coupon Size	0.17	0.091	0.10	0.48	0.83	0.62	0.023

Note: [a] $p < 0.01$ indicates statistical significance; statistically significant values are highlighted and in bold font.

Table 6. Average[a] Recoveries (%) for CWA, Pesticides, and Surrogates from Laminate

Analyte	Direct extraction small	KC DCM small	KC IPA small	KC DCM large	KC IPA large	Dukal DCM small	Dukal IPA small	Dukal DCM large	Dukal IPA large
GB	10 ± 2	ND	ND	ND	ND	ND	ND	ND	ND
GD	14 ± 5	ND	ND	ND	ND	ND	ND	ND	ND
HD	14 ± 4	ND	ND	ND	ND	ND	ND	ND	ND
GF	26 ± 7	ND	ND	ND	ND	ND	ND	ND	ND
VX	50 ± 12	38 ± 8	41 ± 18	31 ± 2	37 ± 6	51 ± 6	25 ± 20 [c]	30 ± 4	26 ± 6
MA	100 ± 17	80 ± 18	66 ± 26	69 ± 5	71 ± 7	69 ± 2	59 ± 20	71 ± 9	50 ± 1
DZN	74 ± 10	51 ± 7	39 ± 12	45 ± 1	44 ± 4	43 ± 7	33 ± 9	47 ± 6	38 ± 5
NB-d_5	ND	93 ± 4	60 ± 8	87 ± 3	95 ± 7	77 ± 34 [c]	39 ± 2	87 ± 10	100 ± 3
2-FB	6 ± 5 [b]	84 ± 3	60 ± 7	84 ± 5	89 ± 3	73 ± 7	70 ± 1	87 ± 9	94 ± 3
PCP- d_5	60 ± 10	85 ± 2	76 ± 4	72 ± 3	88 ± 3	84 ± 6	80 ± 3	82 ± 9	96 ± 3
ter-d_{14}	104 ± 16	99 ± 3	81 ± 4	85 ± 7	93 ± 6	92 ± 5	83 ± 4	89 ± 8	94 ± 2

small = 10 cm^2 coupon spiked with 1 µg analyte; large = 100 cm^2 coupon spiked with 10 µg analyte

Abbreviations: 2-FB = 2-fluorobiphenyl, DCM = dichloromethane, DZN = diazinon, IPA = isopropanol, KC = Kendall-Curity wipe, MA = malathion, NB-d_5 = deuterated nitrobenzene, ND = non-detect, PCP- d_5 = deuterated phencyclidine, ter-d_{14}= deuterated terphenyl

Note: [a] average of three replicates ± the standard deviation of the measurements; [b] estimated concentration was below lowest calibration level; [c] one of the three recoveries was noticeably lower than the others

Table 7. Statistical Analyses (ANOVA p-values [a]) of CWA and Pesticide Recoveries (Table 6) from Laminate

Tested Variable(s)	ANOVA p-values [a]						
	GB	**GD**	**HD**	**GF**	**VX**	**MA**	**DZN**
Wipe	Too few detections for statistical analysis	Too few detections for statistical analysis	Too few detections for statistical analysis	Too few detections for statistical analysis	0.44	0.18	0.13
Wetting Solvent					0.26	0.13	0.014
Coupon Size					0.10	0.64	0.51
Wipe + Wetting Solvent					0.047	0.49	0.59
Wipe + Coupon Size					0.66	0.95	0.51
Wetting Solvent + Coupon Size					0.17	0.84	0.32
Wipe + Wetting Solvent + Coupon Size					0.34	0.34	0.41

Note: [a] $p < 0.01$ indicates statistical significance; statistically significant values are highlighted and in bold font.

Coated glass. GB and GD were not recovered from coated glass under any of the sampling conditions, most likely due to volatilization (Table 8). Only 20 % of the applied HD was recovered by direct extraction from a coated glass coupon and recoveries for HD were < 20 % for all other wipe sampling experiments. Recoveries for VX, malathion, and diazinon were > 50 % for the coated glass surface.

ANOVA analyses could not be performed for GB, GD, and HD, as too many non-detects were observed resulting in insufficient data. ANOVA analyses for GF, VX, malathion, and diazinon was performed based on coupon size. The analyses produced statistically significant differences in recoveries for GF, VX, and malathion (note that the statistical test for diazinon produced a p-value of 0.01; p-values just below this number indicate statistical significance) (Table 9). For VX, malathion, and diazinon, wetting solvent and coupon size produced significant differences.

Wood. CWA and pesticide recoveries from the tested wood surface were low when the surface was directly extracted and non-detectable by wipe extraction. Due to the poor recoveries from the analytes spiked onto this matrix, no statistical analyses could be performed.

Table 8. Average[a] Recoveries (%) for CWA, Pesticides, and Surrogates from Coated Glass

Analyte	Direct extraction small	KC DCM small	KC IPA small	KC DCM large	KC IPA large	Dukal DCM small	Dukal IPA small	Dukal DCM large	Dukal IPA large
GB	ND	ND	ND	ND	ND	ND	ND	ND	ND
GD	ND	ND	ND	ND	ND	ND	ND	ND	ND
HD	20 ± 4	3 ± 5 [b,c]	ND	9 ± 1 [b]	ND	ND	ND	3 ± 5 [b,c]	ND
GF	16 ± 2	15 ± 2	13 ± 0	25 ± 4	19 ± 6	ND	ND	21 ± 7	15 ± 1
VX	51 ± 7	63 ± 10	96 ± 16	83 ± 6	70 ± 8	69 ± 10	102 ± 17	81 ± 9	36 ± 6
MA	104 ± 5	92 ± 4	109 ± 9	101 ± 5	49 ± 8	102 ± 12	107 ± 15	92 ± 7	28 ± 10
DZN	71 ± 13	76 ± 4	71 ± 13	92 ± 4	52 ± 7	77 ± 9	85 ± 15	87 ± 6	38 ± 4
NB-d_5	20 ± 7	76 ± 4	61 ± 1	95 ± 4	66 ± 8	91 ± 7	71 ± 17	92 ± 3	83 ± 3
2-FB	16 ± 3	70 ± 3	69 ± 3	85 ± 3	136 ± 2	78 ± 6	78 ± 10	86 ± 2	77 ± 4
PCP- d_5	69 ± 7	72 ± 1	84 ± 1	82 ± 2	108 ± 1	82 ± 10	95 ± 11	88 ± 3	79 ± 4
ter-d_{14}	82 ± 8	78 ± 2	83 ± 5	90 ± 2	117 ± 1	90 ± 9	90 ± 1	91 ± 4	74 ± 4

small = 10 cm^2 coupon spiked with 1 µg analyte; large = 100 cm^2 coupon spiked with 10 µg analyte

Abbreviations: 2-FB = 2-fluorobiphenyl, DCM = dichloromethane, DZN = diazinon, IPA = isopropanol, KC = Kendall-Curity wipe, MA = malathion, NB-d_5 = deuterated nitrobenzene, ND = non-detect, PCP- d_5 = deuterated phencyclidine, ter-d_{14}= deuterated terphenyl

Note: [a] average of three replicates ± the standard deviation of the measurements; [b] estimated concentration was below lowest calibration level; [c] two of three measurements were "non-detects"

Table 9. Statistical Analyses (ANOVA p-values [a]) of CWA and Pesticide Recoveries (Table 8) from Coated Glass

Tested Variable(s)	ANOVA p-values [a]						
	GB	**GD**	**HD**	**GF**	**VX**	**MA**	**DZN**
Wipe	Too few detections for statistical analysis	Too few detections for statistical analysis	Too few detections for statistical analysis	0.011	0.19	0.15	0.75
Wetting Solvent				0.025	0.66	**<0.0001**	**<0.0001**
Coupon Size				**0.0003**	**0.0038**	**<0.0001**	0.010
Wipe + Wetting Solvent				0.39	0.10	0.13	0.79
Wipe + Coupon Size				0.047	0.017	0.022	0.32
Wetting Solvent + Coupon Size				0.11	**<0.0001**	**<0.0001**	**<0.0001**
Wipe + Wetting Solvent + Coupon Size				0.62	0.099	0.97	0.16

Note: [a] $p < 0.01$ indicates statistical significance; statistically significant values are highlighted and in bold font.

Table 10. Average[a] Recoveries (%) for CWA, Pesticides, and Surrogates[b] from Wood

Analyte	Direct extraction small	KC DCM small	KC IPA small	KC DCM large	KC IPA large	Dukal DCM small	Dukal IPA small	Dukal DCM large	Dukal IPA large
GB	ND	ND	ND	ND	ND	ND	ND	ND	ND
GD	37 ± 8	ND	ND	ND	ND	ND	ND	ND	ND
HD	33 ± 6	ND	ND	ND	ND	ND	ND	ND	ND
GF	60 ± 13	ND	ND	ND	ND	ND	ND	ND	ND
VX	80 ± 40	ND	58 ± 8	ND	ND	ND	21 ± 8	ND	ND
MA	173 ± 1[c]	17 ± 1	44 ± 11	ND	ND	ND	ND	ND	ND
DZN	130 ± 7	14 ± 1	34 ± 6	ND	ND	ND	ND	ND	ND
NB-d_5	74 ± 21	102 ± 9	91 ± 1	91 ± 3	ND	94 ± 3	71 ± 8	100 ± 5	99 ± 1
2-FB	34 ± 7	92 ± 3	98 ± 2	90 ± 3	100 ± 6	90 ± 5	118 ± 2	94 ± 3	96 ± 1
ter-d_{14}	88 ± 6	119 ± 3	112 ± 2	84 ± 2	101 ± 7	101 ± 1	123 ± 3	83 ± 1	89 ± 2

small = 10 cm^2 coupon spiked with 1 µg analyte; large = 100 cm^2 coupon spiked with 10 µg analyte

Abbreviations: 2-FB = 2-fluorobiphenyl, DCM = dichloromethane, DZN = diazinon, IPA = isopropanol, KC = Kendall-Curity wipe, MA = malathion, NB-d_5 = deuterated nitrobenzene, ND = non-detect, PCP- d_5 = deuterated phencyclidine, ter-d_{14}= deuterated terphenyl

Note: [a] average of three replicates ± the standard deviation of the measurements; [b] deuterated phencyclidine was not used in this experiment; [c] interference noted

4.3 Recoveries from Direct Extraction versus Wipe Sampling

Average recoveries for CWAs and pesticides by direct extraction of the matrices and those obtained by wipe sampling of the small coupons were compared using ANOVA (Tables 3, 5, 7, and 9). The data obtained from the statistical analysis involving coupon size suggests a correlation between direct extraction, potentially coupon size, and analyte recoveries. Therefore, only data from the small coupons (and not the large coupons) were considered in the statistical analysis. ANOVA was used because it allowed the consideration of both wipe type (i.e., Kendall-Curity® and Dukal™) and wetting solvent (DCM and IPA) for the various matrices. Since the analysis produced recovery data with many "non-detects," it was not possible to statistically test a difference between direct extraction of the small coupons and that of wipe sampling using various combinations of solvents and wipes for every comparison. However for several conditions, p-values less than 0.01 were observed, indicating that statistically significant differences were noted (Table 11). The analysis suggests that direct extraction yielded statistically-significant, and higher CWA recoveries, than wipe sampling for the removal of the following analytes and small surface coupons (except for VX on vinyl tile, see Section 4.2):

- GB, from drywall
- GD, from vinyl tile
- HD, from drywall
- GF, from drywall and vinyl tile
- Malathion, from drywall and vinyl tile
- Diazinon, from drywall, vinyl tile, and laminate

Although numerous factors (e.g., sampling size, permeability of the surface, solvent compatibility, volatility, concentration, matrix interferents) may play an important role for recovering CWAs, CWA recoveries via direct extraction may be greater than performing wipe sampling on the same surface material. Therefore, wipe sampling may underestimate CWA concentrations on/in these matrices and a “non-detect” produced by wipe sampling cannot be equated with a lack of CWA in a material. These factors are important to note when attempting to accurately interpret results produced by wipe sampling. Furthermore, direct extraction results may be misleading due to matrix interferences. Careful consideration of extraction solvents, matrix interferences, and other factors described above are important when evaluating and interpreting results.

Table 11. Statistical Analyses (ANOVA p-values [a]) of CWA and Pesticide Recoveries (Table 2) from Direct Extraction and Wipe Extraction (Small Coupons Only)

Tested Variable(s)	ANOVA p-values [a]						
	GB	GD	HD	GF	VX	MA	DZN
Drywall							
Wipe/Direct Extraction	**<0.0001**	0.44	**<0.0001**	**<0.0001**	0.77	**<0.0001**	**<0.0001**
Wetting Solvent	0.19	0.75	0.94	0.22	0.48	**0.0027**	0.032
Wipe + Wetting Solvent	0.24	0.92	0.76	0.43	0.58	0.53	0.39
Vinyl Tile							
Wipe/Direct Extraction	b	**<0.0001**	b	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
Wetting Solvent		**<0.0001**		**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
Wipe + Wetting Solvent		**0.0004**		0.012	0.029	0.73	0.47
Laminate							
Wipe/Direct Extraction	b	b	b	b	0.48	0.11	**0.0007**
Wetting Solvent					0.19	0.34	0.069
Wipe + Wetting Solvent					0.12	0.89	0.88
Coated Glass							
Wipe/Direct Extraction	b	b	b	b	0.010	0.77	0.42
Wetting Solvent					**0.0012**	0.086	0.81
Wipe + Wetting Solvent					0.98	0.30	0.36
Wood							
Wipe/Direct Extraction	b	b	b	b	b	b	b
Wetting Solvent							
Wipe + Wetting Solvent							

Abbreviations: DZN = Diazinon, MA = malathion

Notes: [a] $p < 0.01$ indicates statistical significance; statistically significant results are highlighted and shown in bold font; [b] indicates too few detections for statistical analysis

4.4 Sample Holding Times for CWAs on Dukal™ Wipes

A sample holding time study was previously performed using the Kendall-Curity® gauze (3). The Kendall-Curity® gauze was spiked with CWAs and pesticides (0.1-µg and 1-µg levels), stored in a refrigerator (~ 4 ºC), and extracted and analyzed at various times over the course of a month to establish stability. All agents were detected after 30 days on the Kendall-Curity® gauze at the 0.1 µg per wipe concentration, except GB. Sarin (GB), spiked at 0.1 µg, was never recovered at any time point during the study. This previous study also suggested that the CWAs appeared to be stable over the course of a month at a concentration of 1 µg per wipe. The recommendation from the previous study regarding CWA stability was that analysis, or at least the extraction, of

CWA samples should occur within a week of collection so that measured concentrations of CWA would be within ~80% of their original values; however, depending on the analyte, a holding time of 14 days might also be acceptable.

A similar holding time study was performed with the Dukal™ wipes; however, based on the recommendation for the stability of CWAs on the Kendall-Curity gauze, the length of the holding time study was only up to two weeks. Dukal™ wipes were spiked with a concentration of either 0.1 µg or 1.0 µg for each CWA per wipe, and stored in a refrigerator. A set of three separate wipe samples were extracted and analyzed on Days 0, 2, 7, and 14. CWA concentrations on the Dukal™ wipes are presented in Tables 12 and 14 for each tested day (note that Kendall-Curity® results from Reference 3 are provided for comparison). Similar to the results of the study with the Kendall-Curity® wipes, all of the CWAs spiked on the Dukal™ gauze at 1 µg per wipe, were detectable on Day 14. At Day 14, the concentration of VX was half of its original value, but it still greater than the recovery of VX from the Kendall-Curity wipe on Day 14. (Note that the cause of the low, 0.38 µg, amount of VX measured on the Kendall-Curity gauze on Day 2 in unknown; it might possibly be attributed to hydrolysis caused by water inadvertently introduced into the sample or extraction solvent.) Nonetheless, when VX is a target analyte, the data suggests that both wipes should be analyzed within seven days. At the 0.1 µg spiking level, all of the CWA were detectable at Day 14, with the exception of VX, which was no longer detected at Day 14.

Dunnett's test (7) was performed to compare the CWA amounts measured on the Dukal™ wipes at each time point (i.e., $t > 0$) with the initial measured CWA amounts ($t = 0$). The null hypothesis was that the average CWA concentrations at the later times ($t = 2$, 7, or 14 days) were greater than or equal to the initial CWA concentration. The alternative hypothesis was that one or more average CWA concentrations at a later time was less than the initial CWA concentration (a one-sided test). Results of these comparisons are presented in Tables 13 and 15.

Although each set of experimental conditions was evaluated repeatedly over time, the wipes from which samples were extracted were different. That is, the wipe extraction solution analyzed at any given time point was derived from a different wipe than every other time point. Therefore, the measurements at each time point were statistically independent of those at other time points. At a significance level (α) of 0.01 (a conservative value of $\alpha = 0.01$ was chosen over the commonly used value of $\alpha = 0.05$ to compensate for the increased rate of statistical false positives resulting from multiple applications of Dunnett's test), a statistically significant lower amount of VX was observed for the Dukal™ wipes spiked at 0.1 µg and 1 µg at the Day 14 time point when compared to other days. While statistically significant decreases were observed in GB and HD spiked at 0.1 µg on Day 2 and Day 7, a statistically significant decrease was not observed at these time points for the Dukal™ wipes that were spiked at the 1-µg level. None of the Dukal™ wipes showed a statistically significant decrease in GB or HD on Day 14 when compared to Day 0. Thus, the recommendation that CWA samples should be extracted and analyzed within a week of collection may also be applied to samples collected with Dukal™ wipes. The holding time period established for the Dukal™ wipe was consistent with that of the Kendall-Curity® wipe.

Table 12. Holding Time Study Data, 1 µg Each CWA on Wipes

	Dukal™ Wipe – measured CWA amount[a] (µg)				Kendall-Curity® Wipe[b] – measured CWA amount (µg)			
	Day 0	**Day 2**	**Day 7**	**Day 14**	**Day 0**	**Day 2**	**Day 7**	**Day 14**
GB	1.07 ± 0.04	1.07 ± 0.07	0.97 ± 0.05	1.12 ± 0.12	0.89 ± 0.03	0.89 ± 0.03	0.91 ± 0.03	0.9 ± 0.03
GD	1.51 ± 0.11	1.38 ± 0.11	1.51 ± 0.16	1.42 ± 0.20	0.96 ± 0.03	0.99 ± 0.02	1.02 ± 0.02	1.01 ± 0.02
HD	1.11 ± 0.06	1.16 ± 0.10	1.08 ± 0.07	1.16 ± 0.13	0.94 ± 0.04	0.81 ± 0.02	0.92 ± 0.02	0.82 ± 0.04
GF	1.47 ± 0.13	1.27 ± 0.10	1.26 ± 0.14	1.50 ± 0.17	1.08 ± 0.06	1.15 ± 0.05	1.16 ± 0.02	1.18 ± 0.03
VX	1.02 ± 0.09	0.91 ± 0.06	1.06 ± 0.09	**0.53 ± 0.17**	1.02 ± 0.06	**0.38 ± 0.03**	0.96 ± 0.02	**0.32 ± 0.03**

[a] Average amounts ± standard deviation of the measurements of CWA on three wipes, stored in a VOA vial under refrigeration (2-4 °C) for 0, 2, 7, and 14 days after spiking on Day 0 with 1 µg of each CWA; [b] data from previous study (3). Shaded/bold cells indicate a statistically significant recovery difference from Day 0.

Table 13. Statistical Analysis of Holding Time Study Data, 1 µg Each CWA on Dukal™ Wipes

	p-values [a] from Dunnett's Test 1 µg each CWA on Dukal™ Wipe		
Analyte	$t_2 - t_0$	$t_7 - t_0$	$t_{14} - t_0$
GB	0.769	0.159	0.940
GD	0.319	0.740	0.436
HD	0.900	0.578	0.915
GF	0.123	0.113	0.842
VX	0.293	0.873	**<0.001**

Notes: [a] p-values for comparison of 2, 7, and 14-day time point amounts and the measured amount at the start of the experiment (t=0); p-value < 0.01 [in bold] indicates statistically significant concentration decrease.

Table 14. Holding Time Study Data, 0.1 µg Each CWA on Wipes

	Dukal™ Wipe (µg)				Kendall-Curity® Wipe[a] (µg)			
	Day 0	**Day 2**	**Day 7**	**Day 14**	**Day 0**	**Day 2**	**Day 7**	**Day 14**
GB	0.16 ± 0.01	**0.13 ± 0.00**	**0.12 ± 0.00**	0.21 ± 0.01	ND	ND	ND	ND
GD	0.11 ± 0.01	0.08 ± 0.01	0.10 ± 0.01	0.13 ± 0.01	0.11 ± 0.01	0.12 ± 0.01	0.14 ± 0.01	0.15 ± 0.01
HD	0.14 ± 0.01	**0.10 ± 0.00**	**0.10 ± 0.01**	0.22 ± 0.01	0.10 ± 0.00	0.09 ± 0.03	0.11 ± 0.01	0.08 ± 0.01
GF	0.25 ± 0.10	0.19 ± 0.00	0.19 ± 0.03	0.12 ± 0.10	0.11± 0.01	0.13 ± 0.02	0.13 ± 0.01	0.14± 0.00
VX	0.19 ± 0.00	0.16 ± 0.01	0.13 ± 0.01	**ND**	0.11± 0.01	0.09 ± 0.02	0.10 ± 0.01	0.10± 0.06

[a] Average amounts ± standard deviation of the measurements of CWA on three wipes, stored in a VOA vial under refrigeration (2-4 °C) for 0, 2, 7, and 14 days after spiking on Day 0 with 0.1 µg of each CWA; [b] data from previous study (3). Shaded/bold cells indicate a statistically significant recovery difference from Day 0.

Table 15. Statistical Analysis of Holding Time Study Data, 0.1 µg Each CWA on Dukal™ Wipes

	p-values [a] from Dunnett's Test 0.1 µg each CWA on Dukal™ Wipe		
Analyte	$t_2 - t_0$	$t_7 - t_0$	$t_{14} - t_0$
GB	**0.006**	**<0.001**	1
GD	0.029	0.391	0.974
HD	**0.001**	**0.001**	1
GF	0.073	0.084	0.011
VX	0.221	0.021	**<0.001**

Notes: [a] p-values for comparison of 2, 7, and 14-day time point amounts and the measured amount at the start of the experiment (t=0); p-value < 0.01 [in bold] indicates statistically significant concentration decrease.

4.5 VX-d_{14} as an Extracted Internal Standard

Surrogates and internal standards used in the current CWA method (e.g., Method 8270 surrogates and internal standards [4]) are not similar in chemistry to the CWAs. Furthermore, CWAs deposited on porous surfaces presents numerous complications, from matrix interferences to surface interactions and permeation into the surfaces, making recoveries from these matrix types difficult. VX-d_{14}, synthesized by LLNL, could be used to provide valuable information on some of these complications and potentially allow for more accurate quantification of VX itself. Thus, VX-d_{14} was spiked (at the 1 µg level) onto the investigated surfaces (immediately after the surfaces were spiked with unlabeled CWA) and used to quantify VX. Data comparing VX recoveries, from conventional calibration curves and from the response of the deuterated extracted internal standard (IS) (VX-d_{14} listed as VX by *IS*) are presented in Table 16. In almost all cases, recoveries using the response of VX-d_{14} to calculate VX responses are closer to 100 % (assuming 100 % recovery efficiency, i.e., that 100 % recovery is possible from the matrix) than those that do not use the

deuterated extracted internal standard (i.e., calibration curves). The data suggest that the use of VX-d_{14} allows for a more accurate estimation of VX concentrations at low concentrations or when VX recovery efficiencies are problematic. Spiking an isotopically labelled surrogate onto the surface provided valuable information regarding analyte recoveries and potential matrix interferents with specific surfaces. Experiments involving the spiking of VX-d_{14} onto wipe materials prior to sample processing and wipe extraction are still needed to confirm that VX losses on wipe materials are minimal. However, data collected from the direct extraction of the coupon materials provides an approximation of possible losses from these processes. Based on the data presented in Table 16 (using VX-d_{14}), losses from sample processing procedures appears minimal.

Table 16. Average[a] Recoveries (%) for VX, from Various Matrices, with VX-d_{14} as an Extracted Internal Standard (Listed as VX by *IS*) and without (listed as VX)

	Direct extraction small	KC DCM small	KC IPA small	KC DCM large	KC IPA large	Dukal DCM small	Dukal IPA small	Dukal DCM large	Dukal IPA large
Drywall									
VX	94 ± 20	62 ± 17	41 ± 7	8 ± 1 [b]	27 ± 3	48 ± 29	45 ± 4	ND	11 ± 3
VX *by IS*	90 ± 7 [c]	87 ± 6	80 ± 8	97 ± 8	87 ± 2	100 ± 7	86 ± 7	ND	85 ± 10
Vinyl Tile									
VX	ND	125 ± 3	72 ± 6	19 ± 11	27 ± 7	134 ± 1	62 ± 11	14 ± 2	15 ± 4
VX *by IS*	ND	118 ± 4	129 ± 8	127 ± 6	84 ± 1	114 ± 5	150 ± 9	94 ± 2	106 ± 9
Laminate									
VX	50 ± 12	38 ± 8	41 ± 18	31 ± 2	37 ± 6	51 ± 6	25 ± 20 [d]	30 ± 4	26 ± 6
VX *by IS*	94 ± 5	78 ± 13	64 ± 28 [d]	80 ± 5	75 ± 3	72 ± 15	50 ± 18 [d]	73 ± 4	73 ± 8
Coated Glass									
VX	51 ± 7	63 ± 10	96 ± 16	83 ± 6	70 ± 8	69 ± 10	102 ± 17	81 ± 9	36 ± 6
VX *by IS*	101 ± 9	107 ± 7	97 ± 8	118 ± 2	87 ± 10	105 ± 4	110 ± 4	116 ± 4	91 ± 10
Wood									
VX	80 ± 40	ND	58 ± 8	ND	ND	ND	21 ± 8	ND	ND
VX *by IS*	82 ± 3	57 ± 6	57 ± 5	ND	56 ± 2	63 ± 7	56 ± 2	ND	ND

small = coupon of 10 cm^2 surface area, large=coupon with 100 cm^2 surface area

Abbreviations: DCM=dichloromethane, IPA=isopropanol, KC=Kendall-Curity wipe, ND=not detected.

Note: [a] average of three, independent replicates ± the standard deviation of the measurements; [b] estimated average concentration was below lowest calibration level; [c] average of two values, potential outlier ignored; [d] one of three measurements markedly different from the others.

5.0 Conclusions and Recommendations

It is recommended that both tested gauze wipes (Dukal™ and Kendall-Curity®) be pre-cleaned, by solvent extraction, before use due to contaminants present in both wipe materials that may interfere with the analysis of target analytes (specifically VX). Both wipe materials performed well and maintained their physical integrities during the wipe sampling process. For several of the analyte and surface combinations, the Kendall-Curity® gauze wipes yielded higher analyte recoveries. Several factors, or combinations thereof, may attribute to higher recovery yields when using either wipe, such as larger wipe size, solvent effects, and surface material effects. It is worth noting that after both wipes were cleaned, they possessed similar wipe characteristics and composition based on the signatures presented in the chromatograms from analysis of the materials. Regardless, a larger solvent volume may result in greater recovery efficiencies for the target CWA analytes on the tested porous surfaces based on the data presented in the tables.

Holding time studies conducted with 1 µg of each CWA and pesticide spiked on a Dukal™ wipe, placed in a VOA vial, and refrigerated, suggest that most analytes were stable and could be stored for 14 days. VX was the only exception, which was detected at ~50% of its original concentration after two weeks on the Dukal™ wipe. VX was still within range of its original concentration on Day 7, suggesting that VX is stable over this time period. The results for the Dukal™ wipe were similar to an earlier holding time study with the Kendall-Curity® wipes. Thus, it is recommended that wipe samples containing CWA should be extracted and analyzed within a week of collection.

Wipe recoveries of CWAs and pesticides varied depending on the analyte, surface, and (sometimes) wetting solvent used for wipe sampling. There was no clear preferred combination of wipe and wetting solvent that was optimal for CWA sampling on the various surfaces. In general, recoveries from the surfaces were greater by direct extraction than those obtained by wipe sampling, as evidenced from ANOVA analysis for GB, GF, HD, diazinon, and malathion spiked on painted drywall and GD, HD, VX, diazinon, and malathion spiked on vinyl tile. The more volatile CWAs were not recovered from laminate or coated glass, which are not considered to be as porous as the other tested surfaces. Surrogate recoveries for nitrobenzene-d_5 and 2-fluorobiphenyl, also considered volatile chemicals, were poor when spiked directly on the surfaces during the direct extraction experiments. Surrogate recoveries for these two analytes were much higher when they were spiked directly on the wipes, suggesting that analyte volatility may play an important factor in analyte recovery from the surface. Concentration effects were outside the scope of this study, but may help when attempting to understand and address volatilization and/or permeation of chemicals on a surface. It is likely that the more volatile agents were not detected in measurable quantities because these volatile CWAs do not persist on these surfaces at low concentrations. Only a few of the CWAs or pesticides were recovered to a measureable extent on wood; only VX, diazinon, and malathion were recovered under certain conditions, such as sampling from the small coupons.

Many of the analyte recoveries were, from a statistically significantly standpoint, higher for small coupons (surface area 10 cm^2) than for the large coupons (surface area 100 cm^2). There may be many factors (material type, wipe type, wetting solvent, volatilization, etc.) that can affect analyte recovery from porous surfaces and further investigation is needed to decide if surface area plays a significant role with respect to recovery efficiencies.

The use of VX-d_{14}, to calculate VX quantification, improved recovery values (and were closer to 100 % recovery efficiency) at low concentrations, or when VX recoveries are problematic, than those that did not use the VX-d_{14} extracted internal standard (calibration curve was used instead). Data suggest that the use of a labelled extracted internal standard is desirable for a more accurate quantification of VX on porous surfaces. Spiking an isotopically labelled surrogate onto the surface provided valuable information regarding analyte recoveries and potential matrix interferents (enhancement/suppression effects) with specific surfaces. However, it will not be ideal to spike surfaces directly with a hazardous compound, even if it is spiked below clearance levels. Further investigation is still needed to evaluate the spiking of VX-d_{14} onto wipe materials prior to sample processing and wipe extraction instead of the surface itself. Spiking wipe materials with VX-d_{14} in the lab, prior to sample processing and analysis, will still provide useful information with respect to matrix interferences and analyte recoveries without introducing a hazardous chemical in the field.

Knowing the limitations of wipe sampling for particular surfaces is critical in order to correctly interpret and use the results that wipe sampling provides, with respect to recovery efficiency. Before wipe sampling is performed at a contaminated site, it is essential to understand the data quality objectives and questions that are to be addressed from the sampling efforts. The results from a wipe sampling campaign can only be interpreted in the context of meeting preselected study objective(s) and with an understanding that the agent of interest might still reside, in significant quantities, in and/or under the surface of the material sampled by wiping, especially for porous/permeable surfaces. On such surfaces, a “non-detect” produced by wipe sampling cannot be equated with result that CWA is not present in a material.

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Appendix A: Sample Preparation, Extraction, and Analysis of Chemical Warfare Agents from Porous/Permeable Surfaces

Revision 1

United States Environmental Protection Agency

Cincinnati, OH 45268

Disclaimer

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Abbreviations/Acronyms

2-FB	2-fluorobiphenyl
ANOVA	Analysis of Variance (statistical analysis technique)
AS	Analytical Standard
CAL	Calibration Standard
CCV	Continuing calibration verification
CWA	Chemical Warfare Agent
DCM	Dichloromethane
DZN	Diazinon
EPA	United States Environmental Protection Agency
ERLN	Environmental Response Laboratory Network
GB	Sarin (*O*-Isopropyl methylphosphonofluoridate)
GC	Gas Chromatograph
GC/MS	Gas Chromatography/Mass Spectrometry
GD	Soman (3,3-Dimethyl-2-butyl methylphosphonofluoridate)
GF	Cyclosarin (*O*-Cyclohexyl methylphosphonofluoridate)
HD	Sulfur mustard (distilled) (*Bis*(2-chloroethyl)sulfide)
IDC	Initial Demonstration of Capability
IPA	Isopropanol
IS	Internal Standard
KC	Kendall Curity® Gauze
LFMS	Laboratory Fortified Matrix Spike
LFMSD	Laboratory Fortified Matrix Spike Duplicate
LLNL	Lawrence Livermore National Laboratory
LMB	Laboratory Method Blank
MA	Malathion
MDL	Method Detection Limit
MRL	Method Reporting Limit
MS	Mass Spectrometer
NB-d_5	Nitrobenzene-d_5
ND	Non-detect
NIST	National Institute of Standards and Technology
NMR	Nuclear Magnetic Resonance Spectroscopy
OP	Organophosphorus pesticide
PFTBA	Perfluorotributylamine
P/N	Part Number
PTFE	Polytetrafluoroethylene
QC	Quality Control
SD	Standard Deviation
SDS	Safety Data Sheet
SS	Surrogate Standard
SSS	Stock Standard Solution
ter-d_{14}	Terphenyl-d-$_{14}$

TIC	Total Ion Chromatogram
VOA	Volatile Organic Analysis
v/v	Volume/volume percent
VX	*O*-ethyl-*S*-(2-diisopropylaminoethyl) methylphosphonothioate
VX- d_{14}	Deuterated *O*-ethyl-*S*-(2-diisopropylaminoethyl) methylphosphonothioate

1.0 Introduction

Additional commercially-available materials need to be tested when sampling for Chemical Warfare Agents (CWAs). A Dukal™ gauze wipe was tested for contaminants that might interfere with CWA detection and a two-week long stability study was performed to determine the stability of CWA spiked on a Dukal™ wipe, when stored under refrigerated conditions (2-4 °C). This study is follow-on work stemming from previous collected data (3), which identified Kendall-Curity® gauze as the preferred wipe based on holding time stability studies and contaminants/interferences present in the material.

This investigation tested specific (CWAs), including sarin (GB), soman (GD), cyclosarin (GF), sulfur mustard (HD), and *O*-ethyl-*S*-(2-diisopropylaminoethyl) methylphosphonothioate (VX) on the non-ideal (e.g., porous and permeable) surfaces of drywall, vinyl tile, wood, laminate, and coated glass. Pesticides (diazinon and malathion) were used so that a comparison is possible with existing literature data (1). Experiments included testing with coupons having surface areas of 10 cm^2 and 100 cm^2. The 10-cm^2 coupons were of a size that could easily be extracted in a 2-oz jar (to provide comparative data for CWA recoveries generated by direct extraction) and the 100-cm^2 coupons better represented the area of a surface that might typically be sampled by wipe extraction. In addition, CWA, at a normalized surface concentration of 0.1 µg per cm^2 surface area, were spiked on coupons of the tested surfaces. Wipes were wetted with either dichloromethane (DCM) or isopropanol (IPA) before sampling for CWA. Experimental parameters include multiple wipe types, porous/permeable surfaces, coupon surface area, solvent used to wet the wipe (i.e., wetting solvent), and the utility of VX-d_{14} as an extracted internal standard.

2.0 Scope and Application

The sampling and analysis procedure was derived from an existing procedure (2, 3, 4) and used to determine recovery efficiencies of wipe extracts from CWAs on a surface. CWA and the pesticide wipe recoveries from painted drywall, vinyl tile, laminate, coated glass, and wood surfaces were expected to be analyte-dependent, matrix-dependent, and highly variable due to the properties associated with porous/permeable surfaces. Large (100 cm^2 surface area, spiked with 10 µg each analyte) and small (10 cm^2 surface area, spiked with 1 µg each analyte) coupons included GB, GD, HD, GF, VX, diazinon, and malathion and were investigated using various extraction conditions. Wipe sampling experiments were performed using Kendall-Curity® or Dukal™ wipes and with DCM or IPA as the wetting solvent. The wipe recovery efficiencies apply to the wipes, wetting solvents, and surfaces tested within this procedure and should be viewed as general recoveries for surfaces, as the trend may not apply to all tested analytes and/or matrix.

The analytes considered by this procedure include:

Analyte	Abbreviation	CAS Registry[SM] Number
Sarin (GB), *O*-Isopropyl methylphosphonofluoridate	GB	107-44-8
Soman (GD), 3,3-Dimethyl-2-butyl methylphosphonofluoridate	GD	96-64-0
Sulfur mustard (HD), *Bis*(2-chloroethyl)sulfide	HD	505-60-2
Cyclohexyl sarin (GF), *O*-Cyclohexyl methylphosphonofluoridate	GF	329-99-7
VX, *O*-ethyl *S*-[2-(diisopropylamino)ethyl] methylphosphonothioate	VX	50782-69-9

3.0 Summary of Sampling and Analysis Procedure

Target CWAs were spiked onto various porous/permeable surfaces such as painted drywall, wood, and vinyl tile. Polymer-coated glass and laminate surfaces were also tested. Two different-sized coupons (10 cm^2 and 100 cm^2) from the surfaces were investigated. The smaller coupons were either directly extracted in vials or wiped; the wipes extracted for analysis using an existing procedure for CWAs (2). The larger coupons were wiped and extracted for analysis. Both coupon sizes were wiped with either a Kendall-Curity® or a Dukal™ cotton gauze wipe and the wipe extracts were analyzed by the same analytical procedure. Wetting solvents consisted of either dichloromethane (DCM) or isopropanol (IPA); there was no definitive solvent between the two tested solvents. After the surface was wiped with the appropriate wipe material, the collected wipe sample was spiked with surrogate standards and extracted with dichloromethane, using a shaker table. The resulting sample extract was concentrated, internal standards were added, and the sample was analyzed by gas chromatography/mass spectrometry (GC/MS).

4.0 Definitions

4.1 ANALYSIS BATCH – A set of samples analyzed on the same instrument within a 24-hour period and including no more than 20 field samples, beginning and ending with the analysis of the appropriate continuing calibration verification (CCV) standards. Additional CCVs may be required depending on the number of samples (excluding quality control (QC) samples) in the analysis batch and/or the number of field samples.

4.2 CALIBRATION STANDARD (CAL) – A solution prepared from the analyte stock standard solution (AS) and the surrogate/internal standard(s). The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

4.3 CONTINUING CALIBRATION VERIFICATION (CCV) – A calibration standard containing the method analytes and surrogate standard(s). The CCV is analyzed periodically to verify the accuracy of the existing calibration for those analytes at or near the mid-level concentrations. Low calibration concentrations can be added, in addition to mid-level concentrations, for further accuracy, but are not required.

4.4 EXTRACTION BATCH – A set of up to twenty field samples (excluding QC samples) extracted together using the same solvents and surrogate(s).

4.5 LABORATORY FORTIFIED MATRIX SPIKE (LFMS) – A field sample to which known quantities of the method analytes are added in the laboratory. The LFMS is processed and analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate sample.

4.6 LABORATORY FORTIFIED SAMPLE MATRIX DUPLICATE (LFMSD) – A duplicate of the field sample used to prepare the LFMS. The LFMSD is fortified and analyzed identically to the LFMS. The LFMSD is used to assess method precision when the observed concentrations of method analytes are low.

4.7 LABORATORY METHOD BLANK (LMB) – A blank matrix that is treated exactly the same as a sample including exposure to all glassware, equipment, solvents and reagents, and surrogate standards that are used in the analysis batch. The LMB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

4.8 METHOD DETECTION LIMIT (MDL) – The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

4.9 MINIMUM REPORTING LEVEL (MRL) – The minimum concentration that can be reported as a quantitated value for a method analyte in a sample following analysis. This defined concentration can be no lower than the concentration of the lowest calibration standard for that analyte and can be used only if acceptable QC criteria for this standard are met.

4.10 SAFETY DATA SHEET (SDS) – Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

4.11 SURROGATE STANDARD (SS) – A pure chemical(s) added to a standard solution in a known amount(s) and used to measure the relative response of other method analytes that are components of the same solution. The surrogate standard must be a chemical that is structurally similar to the method analytes, has no potential to be present in samples, and is not a method analyte.

4.12 STOCK STANDARD SOLUTION (SSS) – A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

5.0 Interferences

Procedural interferences can be caused by contaminants in solvents, reagents, glassware and other apparatus that lead to discrete artifacts or elevated baselines in the selected ion current profiles. All of these materials must routinely be demonstrated to be free from interferences by analyzing Laboratory Method Blanks (LMBs) under the same conditions as the samples. Subtraction of blank values from sample results is not performed.

5.1 All reagents and solvents should be of pesticide grade purity or higher to minimize interference problems. All glassware should be cleaned and demonstrated to be free from interferences.

5.2 Matrix interferences may be caused by contaminants from the sample matrix, sampling devices or storage containers. The extent of matrix interferences will vary considerably from sample source to sample source, depending upon variations in the sample matrix. Matrix interferences and contaminants are likely to be present and may have an effect on the recoveries for the analytical procedure. These interferences lead to elevated baselines and artifacts that may be interpreted as false positives. Wipes were pre-cleaned using Soxhlet extraction with dichloromethane prior to use to eliminate possible interferences from the wipe matrix (Figures A-4-6).

6.0 Health and Safety

The toxicity and carcinogenicity of each reagent used in this method have not been defined precisely. For this reason, each chemical compound was treated as a health hazard. GB, GD, GF, and VX are nerve agents; HD is a blister agent. Safety Data Sheets (SDSs) for these chemicals, as well as for the solvents, were reviewed prior to initiating experimental work. Exposure to all chemicals was reduced to the lowest possible level and proper protective equipment was worn for protection of skin, eyes, etc.

Personal protective equipment used included nitrile gloves, laboratory coats, and safety glasses with side shields or goggles. Nitrile gloves were changed frequently, between each operation or after known or suspected contact with hazardous material. All work was performed in chemical fume hoods. Sample manipulations were performed in secondary containment (e.g., photo trays) to allow quick cleanup in the event of a spill. Vial trays were used to hold vials and minimize the potential for tipping.

7.0 Equipment and Supplies

The mention of trade names or commercial products is for illustrative purposes only, and does not constitute an endorsement or exclusive recommendation for use. The products and instrument settings cited here represent those products and settings used during method development and experimental studies. Glassware, reagents, supplies, equipment, and settings other than those listed in this procedure may be used, provided that method performance appropriate for the intended application has been demonstrated and documented.

7.1 GC/MS INSTRUMENT

7.1.1 GAS CHROMATOGRAPHY (GC) SYSTEM – An Agilent (Agilent Technologies, Inc., Santa Clara, CA) 7890 GC analytical system was used and equipped with all required accessories including syringes, solvent degasser, and autosampler.

7.1.2 ANALYTICAL COLUMN – GC Agilent (Agilent Technologies, Inc., Santa Clara, CA) HP-5MS, 30 m x 0.25 mm i.d. x 0.25 µm film thickness

7.1.3 MASS SPECTROMETER (MS) SYSTEM – An Agilent 5975C MS (Agilent Technologies, Inc., Santa Clara, CA) mass spectrometer was used in the development of this method. The GC/MS should be tuned and calibrated, as needed, per the vendor's instructions and specifications.

7.1.4 DATA SYSTEM – The GC/MS should be controlled by software that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The software used with the GC/MS system was MSD ChemStation G1701EA, E.02.02.1431.

7.2 EXTRACTION AND CONCENTRATION APPARATUS

7.2.1 Shaker table, digital pulse mixer (model 099A LC1012, Glas-Col, LLC, Terre Haute, IN)

7.2.2 RapidVap unit, customized to accommodate 40-mL vials (LabConco, Kansas City, MO)

7.2.3 Pierce Reacti-Therm™ III (P/N 18824, heating module equipped with the Pierce Reacti-Therm III, P/N 188 evaporation module, ThermoScientific, Hudson, NH)

7.3 GLASSWARE AND MISCELLANEOUS SUPPLIES

7.3.1 Wipes, 3 in. x 3 in., sterile, cotton gauze (Kendall-Curity, 12-ply, P/N 1903, Tyco Heathcare Group LP, Mansfield, MA) (Figure A-1).

7.3.2 Wipes, 2 in. x 2 in., sterile gauze (sold by Fisher Scientific, Pittsburg, PA, as North Co. by Honeywell, P/N 17986486; it should be noted that the wipe received was a gauze wipe, 2 in. x 2 in, 12-ply, made by Dukal Corp. Ronkonkoma, NY) (Figure A-1).

7.3.3 40-mL VOA vials with PTFE-lined screw caps (P/N 0040-0310-PC, Environmental Sampling Supply, Oakland, CA)

7.3.4 2-mL autosampler vials with silver crimp caps (P/N 5182-0543 for vials and P/N 5183-4499 for caps, Agilent, Santa Clara, CA)

7.3.5 Painted drywall – standard, ½" drywall was obtained as surplus from onsite LLNL facilities and are representative samples from commercial hardware stores. Two coats of combination paint and primer (Ultra-Pure White, Interior Matte, Behr Premium Plus Ultra, acrylic paint, P/N 175001, Behr Corp. Santa Ana, CA) were applied to the drywall (Figure A-2).

7.3.6 Polymer-coated glass – glass coupons were cut from commercial window glass by Livermore Glass Company (Livermore, CA). Once cut, a coating (Prestige coating, P/N PR-70, run number 3024324013, 3M, St. Paul, MN) was applied per manufacturer's instructions (5) (Figure A-2).

7.3.7 Wood – surplus plywood was obtained from onsite LLNL facilities and are representative samples from commercial hardware stores (top layer of solid wood is 3/32" thick) (Figure A-2).

7.3.8 Vinyl tile – 1/8", White (Excelon Sanddrift, P/N VCT 51858-45SF, Armstrong, Lancaster, PA) (Figure A-2).

7.3.9 Laminate tile (laminate countertop) – 3' x 8' sheet, White (Designer White, P/N d354-60, S/O, Wilsonart LLC, Temple, TX) (Figure A-2).

7.3.10 Helium, ultra-high purity (UHP, Airgas, Radnor, PA)

7.3.11 Pipettes, of various volumes (Rainin pipettes from Mettler-Toledo, Columbus, OH). Need to measure variable volumes ranging from 1 µL to 10 mL.

8.0 Reagents and Standards

Laboratories should follow QC procedures to determine when the standards should be replaced. Label all standards and verify the correct grade of solvents. Reagent-grade chemicals should be used, unless otherwise indicated. Traceability of materials and standards are established by the manufacturer's specifications provided at time of purchase. Laboratories should follow established, pre-determined QC protocols and procedures for handling CWAs.

8.1 Solvents and Reagents - Dichloromethane (AMD Chromasolv®, ≥99.8% for GC, P/N 34897-6X1L, Sigma-Aldrich, St. Louis, MO). Isopropanol (anhydrous, 99.5%, P/N 278475-1L, Sigma-Aldrich, St. Louis, MO).

8.2 The following surrogate standards were used: a mixed standard containing nitrobenzene-d_5, 2-fluorobiphenyl, and terphenyl-d_{14}, all at 1000 µg/mL (P/N ERB-076, Cerilliant, Round Rock, TX); phencyclidine-d_5, 1000 µg/mL (P/N P-006, Cerilliant).

8.3 The following internal standards were used 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} (Semivolatile Internal Standard Mix, 2000 µg/mL, P/N 861238, Supelco, Bellefonte, PA).

8.4 CWAs (GB, GD, GF, HD, VX, and VX-d_{14}) were synthesized at LLNL and were used to make a 10 µg/mL solution in DCM. Spiking solutions were made from neat agent in

dichloromethane. The purities of the neat agents were determined by nuclear magnetic resonance spectroscopy (NMR) to be 95%, 95%, 95%, 99%, 96%, and 98% for GB, GD, GF, HD, VX, and VX-d_{14}, respectively.

8.5 Dilute all standards to an appropriate concentration in dichloromethane before use. CWA standards are available to the Environmental Response Laboratory Network (ERLN) labs as solutions of 10 µg/mL each CWA in dichloromethane, sealed in 1-mL ampoules. Surrogates and internal standards may be diluted in quantities that are needed. Specific solutions needed include:

8.5.1 10 µg/mL mixed CWA solution (includes GB, GD, GF, and HD)

8.5.2 10 µg/mL VX solution

8.5.3 100 µg/mL surrogate solution (included nitrobenzene-d_5, 2-fluorobiphenyl, terphenyl-d_{14}, and phencyclidine-d_5)

8.5.4 100 µg/mL internal standard solution

8.5.5 10 µg/mL VX-d_{14} solution (if available)

8.6 The above solutions may be diluted with dichloromethane (DCM) to make 1-mL aliquots of calibration standards, to be used for instrument calibration, as described in the table below.

Calibration Standards and Concentrations in DCM

Calibration Level	µL 10 µg/mL CWA mix	µL 10 µg/mL VX	µL 100 µg/mL surrogate mix	µL 100 µg/mL internal standard mix	µL 10 µg/mL VX-d_{14}	µL DCM
1	10	10	1	10	10	959
2	20	20	2	10	20	928
3	40	40	4	10	40	866
4	80	80	8	10	80	742
5	100	100	10	10	100	680
6	200	200	20	10	200	370

9.0 Sample Collection, Extraction, and Storage

Preparation of Control Samples

This section describes preparation of coupons for wipe sampling as well as the preparation of control wipe samples. If this procedure is being used to measure CWA on collected wipes only, skip preparation of samples described in Sections 9.1 – 9.3 and proceed directly to Section 9.4.

9.1 Preparation of large coupons (equivalent surface coverage of 0.1 µg/cm^2).
Spike large coupons of various materials (10 cm x 10 cm) using fifty 20-µL drops of a solution containing 10 µg/mL each CWA in DCM (total spike amount was 10 µg each CWA). The drops of solution are spread evenly over the surface (see Figure A-3). Allow the DCM solvent to evaporate for approximately 5 minutes prior to wipe sampling.

9.2 Preparation of small coupons (equivalent surface coverage of 0.1 µg/cm^2).
Spike small coupons of various materials (area of approximately 10 cm^2) using five 20-µL drops of a solution containing 10 µg/mL each CWA in DCM (total spike amount was 1 µg each CWA). The drops of solution are spread evenly over the surface (see Figure A-3). Allow the DCM solvent to evaporate for approximately 5 minutes prior to wipe sampling.

9.3 Wipe sampling of prepared coupons.
Saturate each wipe with solvent prior to sampling. The Kendall-Curity® wipes were saturated with 5 mL of solvent and the smaller Dukal™ wipes were saturated with 1.5 mL of solvent (either DCM or IPA). The solvent volume was enough to saturate the wipe material without leaving it (or the surface being sampled) dripping wet. Fold each wipe and hold with forceps prior to wiping the surface (NOTE: Depending on the size of the wipe being used (Figure A-1), more than one fold may be needed. The laboratory should use their best judgement to ensure that pre-determined size and folds are adequate to obtain the data quality objectives. The Dukal™ wipes were folded twice and the Kendall-Curity® wipes were folded four times). Wipe the surface, using a steady pressure, in a "Z" pattern – first in the horizontal direction and then in a vertical direction, with a clean wipe surface being exposed each time. After the first pass in the horizontal direction, invert the wipe and wipe in the vertical direction (Figure A-7).

9.4 Preparation of control wipes
Directly spike wipes with 100 µL of a solution containing 10 µg/mL each CWA in DCM (total spike amount was 1 µg each CWA). Directly extract the prepared wipes in DCM (Section 9.5).

9.5 Extraction Procedure

9.5.1 Place wipe into a 40-mL VOA vial for extraction.

Spike with surrogate standards:

9.5.1.1 For small coupons, spike 10 µL of a surrogate solution with each component at 100 µL/mL onto the wipe. This is the recommended surrogate spike amount when analyzing environmental samples.

9.5.1.2 For large coupons were used, spike 100 µL of a surrogate solution with each component at 100 µL/mL onto the wipe.

9.5.2 Add 15.00 mL of DCM to each VOA vial containing a wipe.

9.5.3 Place vials on shaker table (horizontal orientation). Extract for 15 minutes at 600 rpm.

9.5.4 Transfer sample extracts to clean, 40-mL VOA vials and carefully rinse the original vials with DCM.

9.5.5 Add another 15.00-mL aliquot (total volume) of DCM to each vial containing a wipe.

9.5.6 Extract for 15 minutes at 600 rpm on the shaker table.

9.5.7 Combine resulting sample extract with previously collected aliquot.

9.5.8 Concentrate sample extract using clean nitrogen. A RapidVap unit (70% speed, 30 °C, N_2 pressure of 12-15 psi) was used to bring the sample extract to a volume of approximately 1 mL. Transfer the sample extract to an autosampler vial and reduce to a final concentration volume of 1.0 mL (using a gentle stream of N_2, no heat, with the Reacti-Therm unit).

9.5.9 Add internal standard solution; 10 µL of a solution containing 100 ng/µL each internal standard.

9.5.10 Analyze extracts by GC/MS.

9.6 Sample Storage

9.6.1 Store wipe samples in VOA vials in DCM solvent under refrigerated conditions (Section 14.2). Sample stability on wipes is listed in Tables A-12 and A-14.

10.0 Quality Control

10.1 QC requirements include the performance of an initial demonstration of capability (IDC) and ongoing quality control (QC) requirements that must be met to generate data of acceptable quality when preparing and analyzing samples. This section describes the QC parameters, their required frequencies and performance criteria.

10.2 INITIAL DEMONSTRATION OF CAPABILITY

The IDC must be performed successfully prior to the initiation of analysis of field samples. Prior to conducting an IDC, an acceptable initial calibration must be generated.

10.2.1 INITIAL DEMONSTRATION OF LOW SYSTEM BACKGROUND

Any time new solvents, reagents, filters and autosampler vials are used, the LMB must be demonstrated to be free of contamination. The LMB is used to ensure that analytes of interest or other interferences are not present in the laboratory environment, the solvent, or the apparatus.

NOTE: Good laboratory practices indicate the use of solvent and procedure blanks before and after analyzing a calibration curve for an instrument to ensure that no carryover will occur. If the required criteria (as noted within each laboratory's QC protocol) are not met and samples were not free of contamination, then the source of the contamination should be identified and eliminated before the performance of any analysis.

10.2.2 MINIMUM REPORTING LEVEL (MRL)

Establish a target concentration for the MRL based on the intended use of the method. Establish an Initial Calibration. The lowest CAL standard used to establish the initial calibration must be at or below the MRL concentration. If the MRL concentration is too low, ongoing QC requirements may fail repeatedly, and the MRL must be determined again at a higher concentration. The MRL reported in this study is the lowest calibration level.

10.2.3 CONTINUING CALIBRATION VERIFICATION (CCV)

The CCV is used to check the continued validity of the initial calibration. The CCV is a mid-range calibration standard and the acceptance criterion is ±35% of the expected value(s) for all analytes. If the CCV does not meet the acceptance criteria, it may be reanalyzed. If after reanalysis the ±35% criteria for the CCV are not met, a new calibration curve must be made and used. The CCVs consist of clean solvent that is fortified with a specific concentration of CWA (1 µg/mL each agent). A CCV check should be done at a minimum frequency of once every 8 hours; preferably after every 10 field samples.

10.3 METHOD DETECTION LIMIT (MDL)

The procedure for the determination of the laboratory detection and quantitation limits for the EPA approach follows 40 CFR Part 136, Appendix B. MDLs represent the minimum concentration at which there is a high degree of statistical confidence that, when the method reports that an analyte is present, that analyte is actually present (i.e., a low risk of false positives). MDLs were not calculated in this procedure because they were already calculated as described in the previous method (2).

10.4 ONGOING QC REQUIREMENTS

10.4.1 LABORATORY METHOD BLANK (LMB)

Method blanks are used to determine the background of each particular matrix. An LMB is prepared and analyzed with each extraction batch for confirmation that there are no background contaminants interfering with the identification or quantitation of the target analytes. If there is a contaminant within the retention time window preventing the determination of the target analyte, the source of the contamination should be determined and eliminated before processing samples.

The method blanks undergo the same extraction procedure as authentic samples and are spiked with the surrogate standard; however, the method blanks do not contain the target CWA analyte. One method blank is prepared for each set of samples. The maximum number of samples in a set is 20.

10.4.2 CONTINUING CALIBRATION VERIFICATION CHECK

A CCV check should be performed at a minimum frequency of once every 8 hours; preferably after every 10 field samples. CCVs should be within ±35% of the expected value(s) for all analytes for the data to be considered valid. CCV values should be specified by the sample submitter's data quality objectives or fulfill other QC requirements.

10.4.3 MATRIX SPIKE/LABORATORY FORTIFIED MATRIX SPIKE (LFMS)

A LFMS is analyzed to determine that spike accuracy for a particular sample matrix is not adversely affected by chemical interactions between target analytes and experimental matrix. If a variety of sample matrices are analyzed, performance should be established for each matrix or sample type.

10.4.3.1 When performing sample analyses, it is expected that LFMS and LFMSD samples will be analyzed. LFMS/LFMSDs are representative analyte-free environmental matrices that have been fortified with CWA. These samples are taken through the extraction process to show that the method is capable of detecting the analytes of interest in the relevant matrices. LFMS and LFMSD samples should be prepared for each type of matrix. Records are maintained of the target compound spike analyses, and the average percent recovery (X) and the standard deviation (SD) are calculated. Analyte recoveries may exhibit bias for certain matrices. Acceptable recoveries are 50-150% if a low-level concentration near or at the MRL (within a factor of 3) is used. If the recovery does not fall within this range, check with a CCV or prepare a fresh AS solution for analysis. If the recovery of any analyte still falls outside the designated range and the laboratory performance for that analyte is shown to be in control in the CCVs, the recovery is judged to be matrix-biased. The result for that analyte in the unfortified sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

10.4.4 SURROGATE STANDARD

All samples (CCVs, LMBs, LFMSs, LFMSDs, and CAL standards) are spiked with surrogate standard spiking solution. An average percent recovery of the surrogate compound and the standard deviation of the percent recovery are calculated and updated regularly.

11.0 Instrument Calibration and Standardization

All laboratory equipment should be tuned and calibrated according to manufacturer's protocols. Demonstration and documentation of acceptable mass spectrometer (MS) tuning and initial calibration is necessary prior to sample analysis. Verification of the tuning of the MS must be repeated each time instrument modification/maintenance is performed and prior to analyte calibration. After initial calibration is successful, a CCV should be performed at the beginning and end of each analysis batch.

11.1 INITIAL CALIBRATION FOR ANALYTES

11.1.1 Tune and calibrate using the manufacturer's algorithm. When implementing GC/MS method, ensure that there are at least 10 scans across each peak for optimal precision. GC/MS parameters utilized during development of this procedure are presented in Section 12.3.4.

11.1.2 Establish GC operating conditions that will optimize peak resolution and shape. Suggested GC conditions (listed in Section 12.3.4) may not be optimal for all GC systems.

11.1.3 The initial calibration contains a six-point curve using the analyte concentrations prepared (Section 9.6) (NOTE: The highest concentration of the calibration curve will need to be lowered when analyzing CWA standards in other laboratory settings. Laboratories will be limited by the ability to accept CWA standards at concentrations greater than 10 µg/mL so as to protect worker safety.) The lowest calibration curve standard is at the MRL. The calibration curve and all samples should be analyzed in a low to high concentration regimen so carryover is less of a concern in case the GC thermal cycling does not clean the system adequately between injections. Verify that all analytes have been properly identified and quantified using software programs (Section 12.3.3). Integrate manually, if necessary, in accordance with laboratory quality assurance plans. Depending on the instrument, sensitivity and calibration curve responses may vary. If the polynomial type excludes the point of origin, use a fit weighting of 1/X to give more weighting to the lower concentrations. The coefficient of determination (r^2) of the linear fit should be greater than or equal to 0.98. If one of the calibration standards other than the high or low standard causes the r^2 to be <0.98, this point must be re-injected or a new calibration curve must be analyzed. The r^2 of the quadratic curve should be greater than or equal to 0.99. If one of the calibration standards other than the high or low standards causes the r^2 to be <0.99, follow the same procedure given above for a linear fit. A calibration curve and an instrument blank will be analyzed at the beginning of each batch or daily to ensure instrument stability. When quantitated, each calibration point for each analyte should calculate to be within 70-130% of its true value. The lowest CAL standard should calculate to be within 50-150% of its true value. A new curve will be generated daily. The calibration method is used to quantify all samples.

11.2 QUANTITATION OF ANALYTES

The quantitation of the target analytes is accomplished with quantitation software as it relates to each specific instrument (Section 12.3.3.). The data was collected with the Agilent Chemstation software, which was used for quantification. Peak areas associated for each analyte were compared to those of calibration standards. Because deuterated VX (VX-d_{14}) was synthesized and available for use, VX concentrations were quantitated using the isotopically-labeled VX as well. A calibration range of 0.1/0.2– 1.0/2.0 µg/mL is suggested (note that the mixed CWA standard currently shipped to ERLN laboratories contains 5 µg/mL each GD and HD and 10 µg/mL each GB and GF, which impacts the composition of the calibration curve). Refer to the table (Section 13.1) for the quantitation and qualifying ions and retention times utilized for this procedure.

12.0 Analytical Procedure

12.1 SAMPLE PREPARATION

12.1.1 Samples were collected and stored as described in Section 9. The surrogates are added first, then the DCM solvent is added to the VOA vial.

12.1.2 After extraction, transfer resulting sample extract (via pipette) to a standard, 2-mL autosampler vial.

NOTE: Calibration standards are not filtered.

12.2 SAMPLE ANALYSIS/ANALYTICAL SEQUENCE

12.2.1 Use the same Gas Chromatography/Mass Spectrometry conditions established per guidance described below.

12.2.2 Prepare an analytical batch that includes all QC samples and field samples. The first sample to be analyzed is a 1 µL injection of a blank solvent on column followed by the calibration curve.

12.2.3 Update the calibration file and print a calibration report. Review the report for calibration outliers and make area corrections by manual integration, if necessary and appropriate. If corrections have been made, update the calibration file, noting the changes, and regenerate a calibration report. Alternatively, re-analyze "nonconforming" calibration level(s) and repeat the above procedures.

12.2.4 The first sample analyzed after the calibration curve is an additional blank to ensure there is no carryover. If the initial calibration data are acceptable, begin analyzing samples, including QC and blank samples, at their appropriate frequency injecting the same size aliquots (1 µL) under the same conditions used to analyze CAL standards. The ending CCV must have each analyte concentration within 35% of the calculated true concentration or the affected analytes from that run must

be qualified as estimates or the samples must be re-analyzed with passing criteria to remove the qualification.

12.2.5 If the absolute amount of a target compound exceeds the working range of the GC-MS system, the prepared sample is diluted with DCM solvent and re-analyzed along with additional samples that may have run after the sample known to exceed the calibration range, because of the possibility of carryover. Care must be taken to ensure that there is no carryover of the analyte that has exceeded the calibration range. If the amount of analyte exceeds the calibration range, a blank sample should be analyzed afterward to demonstrate no carryover will occur.

12.2.6 At the conclusion of the data acquisition, use the same software that is used in the calibration procedure to identify peaks of interest from the predetermined retention time windows. Use the data software to examine the ion abundances of the peaks in the chromatogram to identify and compare retention times in the sample chromatogram with the retention time of the corresponding analyte peak in an analyte standard.

12.3 CALIBRATION STANDARDS AND GC/MS INSTRUMENT CONDITIONS

12.3.1 Quantification was based on a six-point calibration curve using CWA standards at 0.1, 0.2, 0.4, 0.8, 1, and 2 ng/µL each agent.

12.3.2 Instrument model and serial number: Agilent 5975C, US10204302

12.3.3 Instrument software/software version: MSD ChemStation G1701EA, E.02.02.1431

12.3.4 Instrumental conditions:

GC conditions:

- Carrier gas: Helium
- Flow control/rate: 0.8 mL/min
- Injection mode: Pulsed splitless (25 psi until 0.5 min, 40 mL/min purge flow to split vent at 0.51 min)
- Injection volume: 1 µL
- Injector temperature: 250 °C
- Column brand/phase: Agilent, HP-5MS UI
- Column Length x ID x Film thickness: 30 m x 0.25 mm x 0.25 µm
- GC temperature program: 40 °C (3 min) – 8 °C/min – 300 °C (3 min)

MS conditions:

- Source temperature: 250 °C
- Transfer line temperature: 280 °C

- Solvent delay time: 3 min
- Ionization mode: electron ionization, 70 eV
- Mass resolution: unit
- Scan range/time: 29–600 *m/z* in 0.4 sec

13.0 Data Analysis and Calculations

13.1 QUALITATIVE AND QUANTITATIVE ANALYSIS

13.1.1 Data is acquired by full-scan mass spectrometry. An external calibration is made by considering the quantification ions for each CWA analyte. Quantitation software is utilized to conduct the quantitation of the target analytes and surrogate standards. The ions of each analyte are used for quantitation and confirmation. Furthermore, VX-d_{14} was used as an extracted internal standard for VX analysis.

CWA Mass Spectrometry Ion Transitions and Retention Times

Analyte	Quant. Ion (m/z)	Qual. Ions (primary) (m/z)	Qual. Ions (secondary) (m/z)	Retention Time (min) conditions in §12.3.4
GB	99	125	81	6.35
GD, peak 1	99	126	82	11.01
GD, peak 2	99	126	82	11.10
HD	109	158	63	13.66
GF	99	67	81	14.20
VX-d_{14}	128	80	141	21.99
VX	114	72	127	22.12

13.1.2 Computer programs used for analysis of data include instrumentation and quantitation software. Manual integration may be necessary for some peak areas if the peak area is not integrated properly (i.e., the integration for the peak is not fully performed by the instrument's software, which will be noticeable by visual inspection of each peak). Inspect all integrated peaks for visible integration errors and manually integrate as necessary to ensure consistent integration of other peaks and/or known calibration peaks. Any manual integration should be carried out by a qualified analyst, noted, and checked against quality control procedures.

13.2 Prior to reporting data, the chromatogram should be reviewed for any incorrect peak identifications. The retention time window of the CWA transitions must be within 5% of the retention time of the analyte standard. If this is not true, the calibration curve needs to be re-analyzed to see if there was a shift in retention times during the analysis and the sample needs to be re-injected. If the retention time is still incorrect in the sample, the analyte is referred to as an unknown. If peaks need to be manually adjusted due to incorrect integration by the program, clarification of where professional judgment was used to alter the peaks should be

documented during the data reduction and verification process.

14.0 Method Performance

14.1 RECOVERIES AND PRECISION FOR MATRIX TYPES

14.1.1 Section 18 lists recoveries and precision of target analytes for all tested matrices.

14.2 STORAGE STABILITY STUDY

14.2.1 Spike CWAs on the wetted wipes (IPA or DCM) and store in closed VOA vials under refrigeration (2-4 ºC). Analyze samples on Days 0, 2, 7, 14 to determine the stability of the analytes during the course of fourteen-day storage. CWAs spiked on DCM-wetted (0.5 mL) Dukal™ wipes were at two different concentrations (1 µg and 0.1 µg). (NOTE: A holding time study was previously performed using CWA on the Kendall-Curity® wipe (3) and compared over the fourteen day study for the two tested wipes (Tables A-12 and A-14)).

15.0 Pollution Prevention

15.1 This method utilizes small volumes of organic solvent and small quantities of analytes, thereby minimizing the potential hazards to both analyst and environment. Nevertheless, proper procedures for handling and disposing hazardous analytes should be described for each laboratory's health and safety and waste management plans.

15.2 For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C., 20036 or on-line at http://www.acs.org/content/dam/acsorg/about/governance/committees/chemicalsafety/publications/less-is-better.pdf (accessed August 15, 2013).

16.0 Waste Management

The analytical procedures described within generate relatively small amounts of waste since only small amounts of reagents and solvents are used. Laboratory waste management practices must be conducted consistent with all applicable rules and regulations, and laboratories should protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance with any sewage discharge permits and regulations is required, particularly the hazardous waste identification rules and land disposal restrictions.

16.1 Each laboratory should determine with federal and local officials how to safely dispose of field and QC samples. Waste containers should be properly labeled to identify the contents. Remember to attach the appropriate chemical waste label, date the beginning of collection before using the container and follow all appropriate federal and local waste disposal requirements.

17.0 References

1) *Sampling of Common Pesticides and PCBs from Inert Surfaces*, EPA/330/1-90-001, October 1989, prepared by B. L. Carr and D. F. Hill, National Enforcement Investigations Center, Denver, CO. Washington DC: Office of Enforcement and Compliance Testing, U.S. Environmental Protection Agency.

2) U.S. Environmental Protection Agency (EPA), 2012. *Selected Analytical Methods for Environmental Restoration Following Homeland Security Events* (SAM). EPA/600/R-12/555 July 2012. Cincinnati, Ohio: United States Environmental Protection Agency, Office of Research and Development, National Homeland Security Research Center

3) *Chemical Warfare Agents Wipe Sampling Collection Efficiencies and Holding Time Studies*, LLNL-TR-450992, Lawrence Livermore National Laboratory, August 2010.

4) *Verification of Methods for Selected Chemical Warfare Agents (CWAs)*, January 2013, U.S. Environmental Protection Agency, EPA/600/R-12/653

5) *3M Window Film FAQs*, Accessed January 4, 2016, URL http://solutions.3m.com/wps/portal/3M/en_US/Window_Film/Solutions/Resources/Resources_List/FAQs/.

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Table A-1. Wipe Contaminants Tentatively Identified by GC/MS; Peaks Numbers Correspond to Those Listed in Figures A-4

Peak	Tentative Identification	Retention Time (min)	Reverse Fit
1	2-(2-ethyoxyethyoxy)ethanol	10.39	967
2	2,4-di-tert-butylphenol	19.62	884
3	butylated hydroxytoluene	19.68	920
4	n-hexadecane	20.85	962
5	n-heptadecane	22.28	924
6	n-octadecane	23.63	943
7	n-hexadecanoic acid	25.73	930
8	n-eicosane	26.13	920
9	n-tricosane	29.50	909
10	n-tetracosane	30.53	959
11	n-pentacosane	31.54	907
12	di-n-octyl phthalate	32.09	856
13	n-hexacosane	32.50	909
14	n-heptacosane	33.41	890
15	n-octacosane	34.30	916
16	n-nonacosane	35.16	887
17	Surfynol 104	18.08	876
18	tributylphosphate	21.61	959
19	Uniplex 108	21.84	869
20	pentadecanal	22.51	915
21	dibutylphthalate	25.78	953
22	docosane	28.43	946

Table A-2. Average[a] Recoveries (%) for CWA, Pesticides, and Surrogates from Painted Drywall

Analyte	Direct extraction small	KC DCM small	KC IPA small	KC DCM large	KC IPA large	Dukal DCM small	Dukal IPA small	Dukal DCM large	Dukal IPA large
GB	57 ± 6	15 ± 12	ND	10 ± 3	6 ± 1 [b]	8 ± 4 [b]	4 ± 4 [b]	ND	10 ± 0
GD	114 ± 19	30 ± 26	24 ± 6	11 ± 3	13 ± 4	18 ± 4	15 ± 1	ND	11 ± 1
HD	82 ± 14	13 ± 7	11 ± 3	10 ± 2	8 ± 1 [b]	8 ± 3 [b]	9 ± 1 [b]	ND	8 ± 0 [b]
GF	115 ± 20	40 ± 20	24 ± 4	5 ± 3 [b]	19 ± 3	27 ± 7	21 ± 1	ND	5 ± 0 [b]
VX	94 ± 20	62 ± 17	41 ± 7	8 ± 1 [b]	27 ± 3	48 ± 29	45 ± 4	ND	11 ± 3
MA	127 ± 9	55 ± 13	17 ± 16	4 ± 1 [b]	9 ± 7 [b]	41 ± 7	17 ± 2	ND	ND
DZN	84 ± 12	41 ± 19	18 ± 5	6 ± 1 [b]	12 ± 3	29 ± 11	18 ± 2	ND	ND
NB-d_5	75 ± 10	57 ± 8	63 ± 5	71 ± 7	ND	74 ± 9	39 ± 3	81 ± 16	89 ± 7
2-FB	69 ± 4	56 ± 9	79 ± 5	78 ± 8	140 ± 0	70 ± 9	83 ± 2	74 ± 5	91 ± 7
PCP-d_5	84 ± 9	88 ± 9	86 ± 10	71 ± 6	140 ± 1	113 ± 8	101 ± 1	67 ± 7	90 ± 7
ter-d_{14}	74 ± 6	59 ± 7	84 ± 7	77 ± 5	150 ± 0	73 ± 11	87 ± 3	72 ± 6	90 ± 6

small = 10 cm^2 coupon spiked with 1 µg analyte; large = 100 cm^2 coupon spiked with 10 µg analyte

Abbreviations: 2-FB = 2-fluorobiphenyl, DCM = dichloromethane, DZN = diazinon, IPA = isopropanol, KC = Kendall-Curity wipe, MA = malathion, NB-d_5 = deuterated nitrobenzene, ND = non-detect, PCP- d_5 = deuterated phencyclidine, ter-d_{14}= deuterated terphenyl

Note: [a] average of three replicates ± the standard deviation of the measurements; [b] estimated average concentration was below lowest calibration level

Table A-3. Statistical Analyses (ANOVA p-values [a]) of CWA and Pesticide Recoveries (Table A-2) from Drywall

Tested Variable(s)	ANOVA p-values [a]						
	GB	**GD**	**HD**	**GF**	**VX**	**MA**	**DZN**
Wipe	0.48	0.10	0.54	0.025	0.19	0.16	0.16
Wetting Solvent	0.21	0.96	0.99	0.63	0.98	**0.0008**	0.087
Coupon Size	0.54	**0.010**	0.11	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
Wipe + Wetting Solvent	0.030	0.70	0.30	0.91	0.84	0.56	0.41
Wipe + Coupon Size	0.62	0.41	0.66	0.78	0.75	0.31	0.95
Wetting Solvent + Coupon Size	0.20	0.31	0.80	0.021	0.32	**<0.0001**	**0.0033**
Wipe + Wetting Solvent + Coupon Size	0.96	0.98	0.96	0.057	0.12	0.27	0.29

Note: [a] $p < 0.01$ indicates statistical significance; statistically significant results are highlighted and in bold font.

Table A-4. Average[a] Recoveries (%) for CWA, Pesticides, and Surrogates from Vinyl Tile

Analyte	Direct extraction small	KC DCM small	KC IPA small	KC DCM large	KC IPA large	Dukal DCM small	Dukal IPA small	Dukal DCM large	Dukal IPA large
GB	59 ± 2	29 ± 5	ND	9 ± 1 [b]	ND	19 ± 1	ND	ND	ND
GD	107 ± 6	72 ± 2	ND	11 ± 3	ND	60 ± 4	7 ± 0 [b]	ND	ND
HD	84 ± 3	43 ± 1	ND	10 ± 3	ND	29 ± 3	ND	ND	ND
GF	114 ± 5	96 ± 2	16 ± 3	20 ± 7	ND	81 ± 4	12 ± 1	ND	ND
VX	ND	125 ± 3	72 ± 6	19 ± 11	27 ± 7	134 ± 1	62 ± 11	14 ± 2	15 ± 4
MA	138 ± 6	104 ± 3	35 ± 2	6 ± 3 [b]	ND	92 ± 2	34 ± 1	ND	ND
DZN	111 ± 5	84 ± 5	23 ± 2	13 ± 6	ND	86 ± 1	22 ± 1	ND	ND
NB-d_5	78 ± 6	56 ± 2	73 ± 9	74 ± 6	76 ± 6	88 ± 11	44 ± 4	117 ± 8	91 ± 2
2-FB	65 ± 4	44 ± 2	87 ± 4	78 ± 5	141 ± 1	78 ± 8	92 ± 10	119 ± 4	88 ± 2
PCP- d_5	41 ± 4	75 ± 2	99 ± 3	76 ± 6	125 ± 1	86 ± 5	109 ± 0	106 ± 3	100 ± 6
ter-d_{14}	53 ± 3	51 ± 3	100 ± 4	81 ± 7	151 ± 1	88 ± 7	95 ±10	131 ± 4	104 ± 6

small = 10 cm^2 coupon spiked with 1 µg analyte; large = 100 cm^2 coupon spiked with 10 µg analyte

Abbreviations: 2-FB = 2-fluorobiphenyl, DCM = dichloromethane, DZN = diazinon, IPA = isopropanol, KC = Kendall-Curity wipe, MA = malathion, NB-d_5 = deuterated nitrobenzene, ND = non-detect, PCP- d_5 = deuterated phencyclidine, ter-d_{14}= deuterated terphenyl

Note: [a] average of three replicates ± the standard deviation of the measurements; [b] estimated average concentration was below lowest calibration level

Table A-5. Statistical Analyses (ANOVA p-values [a]) of CWA and Pesticide Recoveries (Table A-4) from Vinyl Tile

Tested Variable(s)	ANOVA p-values [a]						
	GB	**GD**	**HD**	**GF**	**VX**	**MA**	**DZN**
Wipe	**0.0026**	**0.0088**	**0.0082**	**0.0002**	0.021	0.033	**0.0003**
Wetting Solvent	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
Coupon Size	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
Wipe + Wetting Solvent	**<0.0001**	**0.0031**	**0.0002**	**0.0003**	**0.0043**	0.97	**0.0024**
Wipe + Coupon Size	**<0.0001**	0.40	0.52	0.11	0.034	0.061	**<0.0001**
Wetting Solvent + Coupon Size	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
Wipe + Wetting Solvent + Coupon Size	0.17	0.091	0.10	0.48	0.83	0.62	0.023

Note: [a] $p < 0.01$ indicates statistical significance; statistically significant results are highlighted and in bold font.

Table A-6. Average[a] Recoveries (%) for CWA, Pesticides, and Surrogates from Laminate

Analyte	Direct extraction small	KC DCM small	KC IPA small	KC DCM large	KC IPA large	Dukal DCM small	Dukal IPA small	Dukal DCM large	Dukal IPA large
GB	10 ± 2	ND	ND	ND	ND	ND	ND	ND	ND
GD	14 ± 5	ND	ND	ND	ND	ND	ND	ND	ND
HD	14 ± 4	ND	ND	ND	ND	ND	ND	ND	ND
GF	26 ± 7	ND	ND	ND	ND	ND	ND	ND	ND
VX	50 ± 12	38 ± 8	41 ± 18	31 ± 2	37 ± 6	51 ± 6	25 ± 20 [c]	30 ± 4	26 ± 6
MA	100 ± 17	80 ± 18	66 ± 26	69 ± 5	71 ± 7	69 ± 2	59 ± 20	71 ± 9	50 ± 1
DZN	74 ± 10	51 ± 7	39 ± 12	45 ± 1	44 ± 4	43 ± 7	33 ± 9	47 ± 6	38 ± 5
NB-d_5	ND	93 ± 4	60 ± 8	87 ± 3	95 ± 7	77 ± 34 [c]	39 ± 2	87 ± 10	100 ± 3
2-FB	6 ± 5 [b]	84 ± 3	60 ± 7	84 ± 5	89 ± 3	73 ± 7	70 ± 1	87 ± 9	94 ± 3
PCP- d_5	60 ± 10	85 ± 2	76 ± 4	72 ± 3	88 ± 3	84 ± 6	80 ± 3	82 ± 9	96 ± 3
ter-d_{14}	104 ± 16	99 ± 3	81 ± 4	85 ± 7	93 ± 6	92 ± 5	83 ± 4	89 ± 8	94 ± 2

small = 10 cm^2 coupon spiked with 1 µg analyte; large = 100 cm^2 coupon spiked with 10 µg analyte

Abbreviations: 2-FB = 2-fluorobiphenyl, DCM = dichloromethane, DZN = diazinon, IPA = isopropanol, KC = Kendall-Curity wipe, MA = malathion, NB-d_5 = deuterated nitrobenzene, ND = non-detect, PCP- d_5 = deuterated phencyclidine, ter-d_{14}= deuterated terphenyl

Note: [a] average of three replicates ± the standard deviation of the measurements; [b] estimated concentration was below lowest calibration level; [c] one of the three recoveries was noticeably lower than the others

Table A-7. Statistical Analyses (ANOVA p-values [a]) of CWA and Pesticide Recoveries (Table A-6) from Laminate

Tested Variable(s)	ANOVA p-values [a]						
	GB	**GD**	**HD**	**GF**	**VX**	**MA**	**DZN**
Wipe	Too few detections for statistical analysis	Too few detections for statistical analysis	Too few detections for statistical analysis	Too few detections for statistical analysis	0.44	0.18	0.13
Wetting Solvent					0.26	0.13	0.014
Coupon Size					0.10	0.64	0.51
Wipe + Wetting Solvent					0.047	0.49	0.59
Wipe + Coupon Size					0.66	0.95	0.51
Wetting Solvent + Coupon Size					0.17	0.84	0.32
Wipe + Wetting Solvent + Coupon Size					0.34	0.34	0.41

Note: [a] $p < 0.01$ indicates statistical significance; statistically significant results are in highlighted font.

Table A-8. Average[a] Recoveries (%) for CWA, Pesticides, and Surrogates from Coated Glass

Analyte	Direct extraction small	KC DCM small	KC IPA small	KC DCM large	KC IPA large	Dukal DCM small	Dukal IPA small	Dukal DCM large	Dukal IPA large
GB	ND	ND	ND	ND	ND	ND	ND	ND	ND
GD	ND	ND	ND	ND	ND	ND	ND	ND	ND
HD	20 ± 4	3[b,c]	ND	9 ± 1 [b]	ND	ND	ND	3 [b,c]	ND
GF	16 ± 2	15 ± 2	13 ± 0	25 ± 4	19 ± 6	ND	ND	21 ± 7	15 ± 1
VX	51 ± 7	63 ± 10	96 ± 16	83 ± 6	70 ± 8	69 ± 10	102 ± 17	81 ± 9	36 ± 6
MA	104 ± 5	92 ± 4	109 ± 9	101 ± 5	49 ± 8	102 ± 12	107 ± 15	92 ± 7	28 ± 10
DI	71 ± 13	76 ± 4	71 ± 13	92 ± 4	52 ± 7	77 ± 9	85 ± 15	87 ± 6	38 ± 4
NB-d_5	20 ± 7	76 ± 4	61 ± 1	95 ± 4	66 ± 8	91 ± 7	71 ± 17	92 ± 3	83 ± 3
2-FB	16 ± 3	70 ± 3	69 ± 3	85 ± 3	136 ± 2	78 ± 6	78 ± 10	86 ± 2	77 ± 4
PCP- d_5	69 ± 7	72 ± 1	84 ± 1	82 ± 2	108 ± 1	82 ± 10	95 ± 11	88 ± 3	79 ± 4
ter-d_{14}	82 ± 8	78 ± 2	83 ± 5	90 ± 2	117 ± 1	90 ± 9	90 ± 1	91 ± 4	74 ± 4

small = 10 cm^2 coupon spiked with 1 µg analyte; large = 100 cm^2 coupon spiked with 10 µg analyte

Abbreviations: 2-FB = 2-fluorobiphenyl, DCM = dichloromethane, DZN = diazinon, IPA = isopropanol, KC = Kendall-Curity wipe, MA = malathion, NB-d_5 = deuterated nitrobenzene, ND = non-detect, PCP- d_5 = deuterated phencyclidine, ter-d_{14}= deuterated terphenyl

Note: [a] average of three replicates ± the standard deviation of the measurements; [b] estimated concentration was below lowest calibration level; [c] two of three measurements were "non-detects"

Table A-9. Statistical Analyses (ANOVA p-values[a]) of CWA and Pesticide Recoveries (Table A-8) from Coated Glass

Variable(s) Tested	ANOVA p-values [a]						
	GB	**GD**	**HD**	**GF**	**VX**	**MA**	**DZN**
Wipe	Too few detections for statistical analysis	Too few detections for statistical analysis	Too few detections for statistical analysis	0.011	0.19	0.15	0.75
Wetting Solvent				0.025	0.66	**<0.0001**	**<0.0001**
Coupon Size				**0.0003**	**0.0038**	**<0.0001**	0.010
Wipe + Wetting Solvent				0.39	0.10	0.13	0.79
Wipe + Coupon Size				0.047	0.017	0.022	0.32
Wetting Solvent + Coupon Size				0.11	**<0.0001**	**<0.0001**	**<0.0001**
Wipe + Wetting Solvent + Coupon Size				0.62	0.099	0.97	0.16

Note: [a] $p < 0.01$ indicates statistical significance; statistically significant results are highlighted and in bold font.

Table A-10. Average[a] Recoveries (%) for CWA, Pesticides, and Surrogates[b] from Wood

Analyte	Direct extraction small	KC DCM small	KC IPA small	KC DCM large	KC IPA large	Dukal DCM small	Dukal IPA small	Dukal DCM large	Dukal IPA large
GB	ND	ND	ND	ND	ND	ND	ND	ND	ND
GD	37 ± 8	ND	ND	ND	ND	ND	ND	ND	ND
HD	33 ± 6	ND	ND	ND	ND	ND	ND	ND	ND
GF	60 ± 13	ND	ND	ND	ND	ND	ND	ND	ND
VX	80 ± 40	ND	58 ± 8	ND	ND	ND	21 ± 8	ND	ND
MA	173 ± 1[c]	17 ± 1	44 ± 11	ND	ND	ND	ND	ND	ND
DZN	130 ± 7	14 ± 1	34 ± 6	ND	ND	ND	ND	ND	ND
NB-d_5	74 ± 21	102 ± 9	91 ± 1	91 ± 3	ND	94 ± 3	71 ± 8	100 ± 5	99 ± 1
2-FB	34 ± 7	92 ± 3	98 ± 2	90 ± 3	100 ± 6	90 ± 5	118 ± 2	94 ± 3	96 ± 1
ter-d_{14}	88 ± 6	119 ± 3	112 ± 2	84 ± 2	101 ± 7	101 ± 1	123 ± 3	83 ± 1	89 ± 2

small = 10 cm^2 coupon spiked with 1 µg analyte; large = 100 cm^2 coupon spiked with 10 µg analyte

Abbreviations: 2-FB = 2-fluorobiphenyl, DCM = dichloromethane, DZN = diazinon, IPA = isopropanol, KC = Kendall-Curity wipe, MA = malathion, NB-d_5 = deuterated nitrobenzene, ND = non-detect, PCP- d_5 = deuterated phencyclidine, ter-d_{14}= deuterated terphenyl

Note: [a] average of three replicates ± the standard deviation of the measurements; [b] deuterated phencyclidine was not used in this experiment; [c] interference noted

Table A-11. Statistical Analyses (ANOVA p-values [a]) of CWA and Pesticide Recoveries from Direct Extraction and Wipe Extraction (Small Coupons Only)

Tested Variable(s) per Matrix	ANOVA p-values [a]						
	GB	**GD**	**HD**	**GF**	**VX**	**MA**	**DZN**
Drywall							
Wipe/Direct Extraction	**<0.0001**	0.44	**<0.0001**	**<0.0001**	0.77	**<0.0001**	**<0.0001**
Wetting Solvent	0.19	0.75	0.94	0.22	0.48	**0.0027**	0.032
Wipe + Wetting Solvent	0.24	0.92	0.76	0.43	0.58	0.53	0.39
Vinyl Tile							
Wipe/Direct Extraction	b	**<0.0001**	b	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
Wetting Solvent		**<0.0001**		**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
Wipe + Wetting Solvent		**0.0004**		0.012	0.029	0.73	0.47
Laminate							
Wipe/Direct Extraction	b	b	b	b	0.48	0.11	**0.0007**
Wetting Solvent					0.19	0.34	0.069
Wipe + Wetting Solvent					0.12	0.89	0.88
Coated Glass							
Wipe/Direct Extraction	b	b	b	b	0.010	0.77	0.42
Wetting Solvent					**0.0012**	0.086	0.81
Wipe + Wetting Solvent					0.98	0.30	0.36
Wood							
Wipe/Direct Extraction	b	b	b	b	b	b	b
Wetting Solvent							
Wipe + Wetting Solvent							

Abbreviations: DZN = diazinon, MA = malathion

Notes: [a] $p < 0.01$ indicates statistical significance; statistically significant results highlighted and in bold font. [b] indicates too few detections for statistical analysis

Table A-12. Holding Time Study Data, 1 µg Each CWA on Wipes

	Dukal™ Wipe – measured CWA amount				Kendall-Curity® Wipe [a] – measured CWA amount			
	Day 0	**Day 2**	**Day 7**	**Day 14**	**Day 0**	**Day 2**	**Day 7**	**Day 14**
GB	1.07 ± 0.04	1.07 ± 0.07	0.97 ± 0.05	1.12 ± 0.12	0.89 ± 0.03	0.89 ± 0.03	0.91 ± 0.03	0.9 ± 0.03
GD	1.51 ± 0.11	1.38 ± 0.11	1.51 ± 0.16	1.42 ± 0.20	0.96 ± 0.03	0.99 ± 0.02	1.02 ± 0.02	1.01 ± 0.02
HD	1.11 ± 0.06	1.16 ± 0.10	1.08 ± 0.07	1.16 ± 0.13	0.94 ± 0.04	0.81 ± 0.02	0.92 ± 0.02	0.82 ± 0.04
GF	1.47 ± 0.13	1.27 ± 0.10	1.26 ± 0.14	1.50 ± 0.17	1.08 ± 0.06	1.15 ± 0.05	1.16 ± 0.02	1.18 ± 0.03
VX	1.02 ± 0.09	0.91 ± 0.06	1.06 ± 0.09	**0.53 ± 0.17**	1.02 ± 0.06	**0.38 ±0.03[b]**	0.96 ± 0.02	**0.32 ± 0.03**

Average amounts ± standard deviation of the measurements of CWA on three wipes, stored in a VOA vial under refrigeration (2-4 °C) for 0, 2, 7, and 14 days after spiking on Day 0 with 1 µg of each CWA.

[a] data from previous study (3); [b] cause of the low, 0.38 µg, amount of VX measured on the Kendall-Curity gauze on Day 2 in unknown; possible causes might be attributed to hydrolysis (e.g., water inadvertently introduced into the sample or extraction solvent).

Table A-13. Statistical Analysis of Holding Time Study Data, 1 µg Each CWA on Dukal™ Wipes

	p-values [a] from Dunnett's Test 1 µg each CWA on Dukal™ Wipe		
Analyte	$t_2 - t_0$	$t_7 - t_0$	$t_{14} - t_0$
GB	0.769	0.159	0.940
GD	0.319	0.740	0.436
HD	0.900	0.578	0.915
GF	0.123	0.113	0.842
VX	0.293	0.873	**<0.001**

Notes: [a] p-values for comparison of 2, 7, and 14-day time point amounts and the measured amount at the start of the experiment (t=0); p-value < 0.01 indicates statistically significant concentration decrease.

Table A-14. Holding Time Study Data, 0.1 µg Each CWA on Wipes

	Dukal™ Wipe [a]				Kendall-Curity® Wipe [b]			
	Day 0	**Day 2**	**Day 7**	**Day 14**	**Day 0**	**Day 2**	**Day 7**	**Day 14**
GB	0.16 ± 0.01	**0.13 ± 0.00**	**0.12 ± 0.00**	0.21 ± 0.01	ND	ND	ND	ND
GD	0.11 ± 0.01	0.08 ± 0.01	0.10 ± 0.01	0.13 ± 0.01	0.11 ± 0.01	0.12 ± 0.01	0.14 ± 0.01	0.15 ± 0.01
HD	0.14 ± 0.01	**0.10 ± 0.00**	**0.10 ± 0.01**	0.22 ± 0.01	0.10 ± 0.00	0.09 ± 0.03	0.11 ± 0.01	0.08 ± 0.01
GF	0.25 ± 0.10	0.19 ± 0.00	0.19 ± 0.03	0.12 ± 0.10	0.11± 0.01	0.13 ± 0.02	0.13 ± 0.01	0.14± 0.00
VX	0.19 ± 0.00	0.16 ± 0.01	0.13 ± 0.01	**ND**	0.11± 0.01	0.09 ± 0.02	0.10 ± 0.01	0.10± 0.06

[a] Average amounts ± standard deviation of the measurements of CWA on three wipes, stored in a VOA vial under refrigeration (2-4 °C) for 0, 2, 7, and 14 days after spiking on Day 0 with 0.1 µg of each CWA; [b] data from previous study (3)

Table A-15. Statistical Analysis of Holding Time Study Data, 0.1 µg Each CWA on Dukal™ Wipes

	p-values [a] from Dunnett's Test 0.1 µg each CWA on Dukal™ Wipe		
Analyte	**$t_2 - t_0$**	**$t_7 - t_0$**	**$t_{14} - t_0$**
GB	**0.006**	**<0.001**	1
GD	0.029	0.391	0.974
HD	**0.001**	**0.001**	1
GF	0.073	0.084	0.011
VX	0.221	0.021	**<0.001**

Notes: [a] p-values for comparison of 2, 7, and 14-day time point amounts and the measured amount at the start of the experiment (t=0); p-value < 0.01 indicates statistically significant concentration decrease.

Table A-16. Average[a] Recoveries (%) for VX, from Various Matrices, With and Without Consideration of VX-d_{14} Extracted Internal Standard (Listed as VX *by IS*).

Matrix	Direct extraction small	KC DCM small	KC IPA small	KC DCM large	KC IPA large	Dukal DCM small	Dukal IPA small	Dukal DCM large	Dukal IPA large
Drywall									
VX	94 ± 20	62 ± 17	41 ± 7	8 ± 1 [b]	27 ± 3	48 ± 29	45 ± 4	ND	11 ± 3
VX *by IS*	90 ± 7 [c]	87 ± 6	80 ± 8	97 ± 8	87 ± 2	100 ± 7	86 ± 7	ND	85 ± 10
Vinyl Tile									
VX	ND	125 ± 3	72 ± 6	19 ± 11	27 ± 7	134 ± 1	62 ± 11	14 ± 2	15 ± 4
VX *by IS*	ND	118 ± 4	129 ± 8	127 ± 6	84 ± 1	114 ± 5	150 ± 9	94 ± 2	106 ± 9
Laminate									
VX	50 ± 12	38 ± 8	41 ± 18	31 ± 2	37 ± 6	51 ± 6	25 ± 20 [d]	30 ± 4	26 ± 6
VX *by IS*	94 ± 5	78 ± 13	64 ± 28 [d]	80 ± 5	75 ± 3	72 ± 15	50 ± 18 [d]	73 ± 4	73 ± 8
Coated Glass									
VX	51 ± 7	63 ± 10	96 ± 16	83 ± 6	70 ± 8	69 ± 10	102 ± 17	81 ± 9	36 ± 6
VX *by IS*	101 ± 9	107 ± 7	97 ± 8	118 ± 2	87 ± 10	105 ± 4	110 ± 4	116 ± 4	91 ± 10
Wood									
VX	80 ± 40	ND	58 ± 8	ND	ND	ND	21 ± 8	ND	ND
VX *by IS*	82 ± 3	57 ± 6	57 ± 5	ND	56 ± 2	63 ± 7	56 ± 2	ND	ND

small=coupon of 10 cm^2 surface area, large=coupon with 100 cm^2 surface area

Abbreviations: DCM=dichloromethane, IPA=isopropanol, KC=Kendall-Curity wipe

Note: [a] average of three, independent replicates ± the standard deviation of the measurements; [b] estimated average concentration was below lowest calibration level; [c] average of two values, potential outlier ignored; [d] one of three measurements markedly different from the others

Figure A-1. Kendall-Curity® wipe (left) and Dukal™ wipe (right).

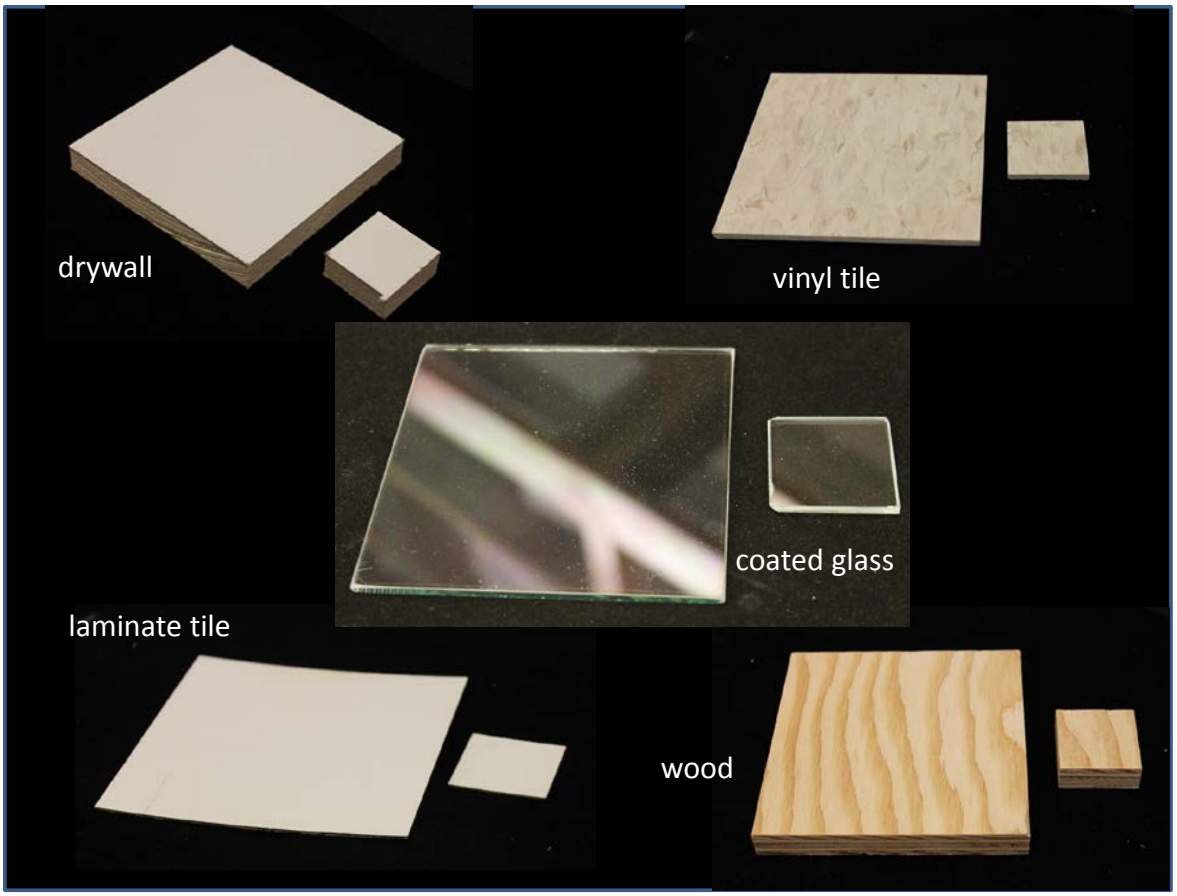

Figure A-2. Materials tested in this study (100 cm^2 and 10 cm^2 coupons).

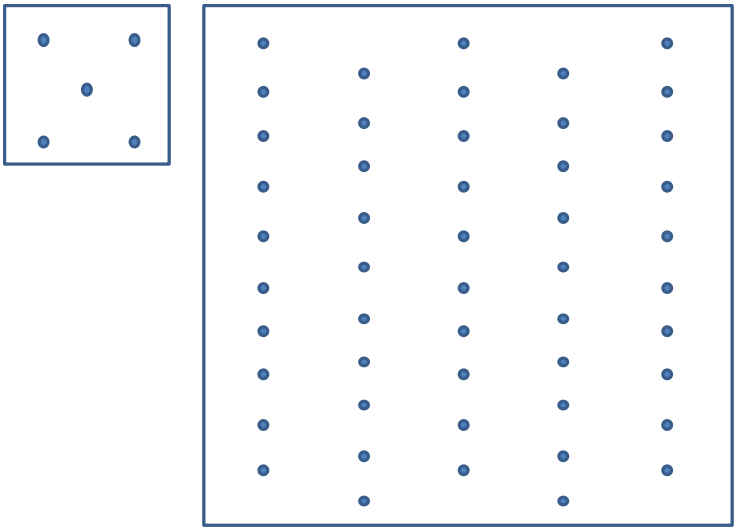

Figure A-3. Example spiking patterns for 10-cm^2 and 100-cm^2 coupons.

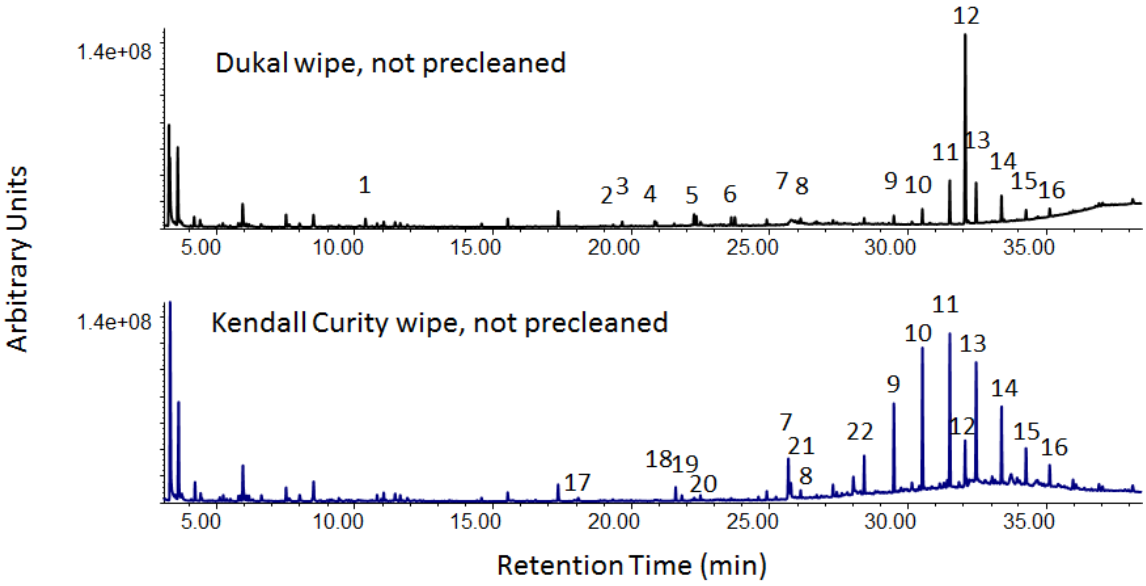

Figure A-4. TICs for wipes that were received, extracted, and analyzed by GC/MS. Compounds were tentatively identified by library search and summarized in Table A-1.

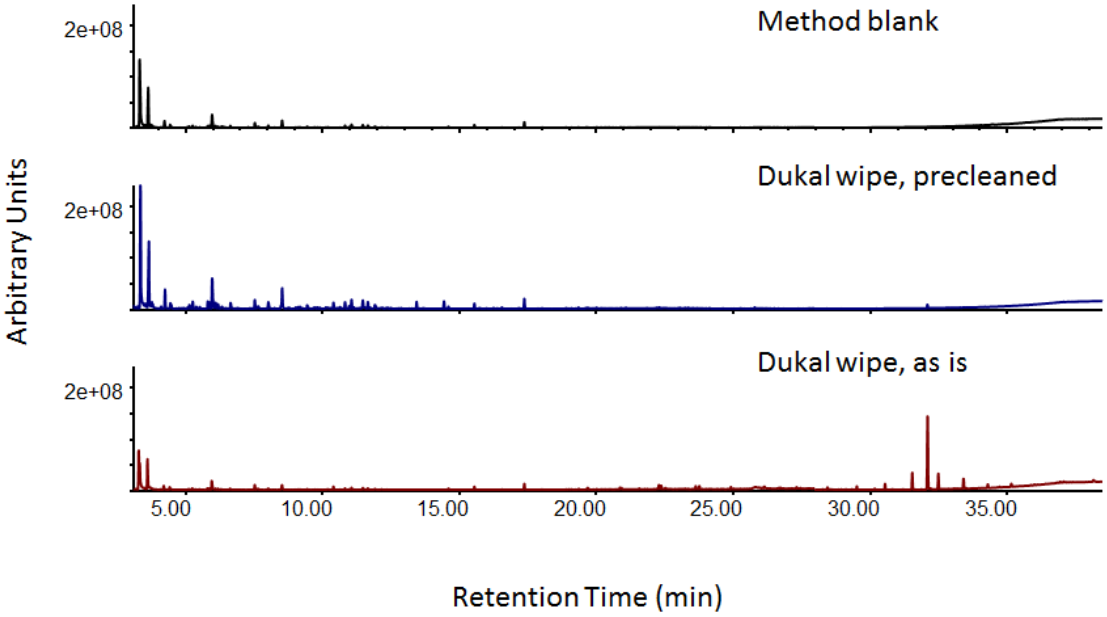

Figure A-5. TICs for method blank and Dukal wipes pre-cleaned and "as received".

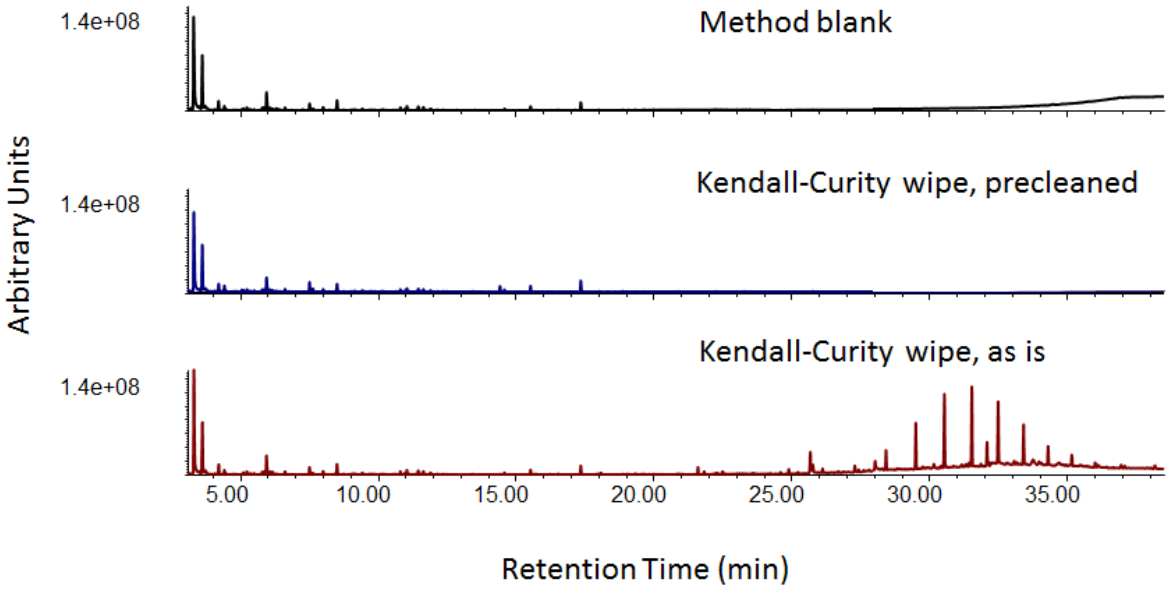

Figure A-6. TICs for method blank and Kendall-Curity wipes pre-cleaned and "as received".

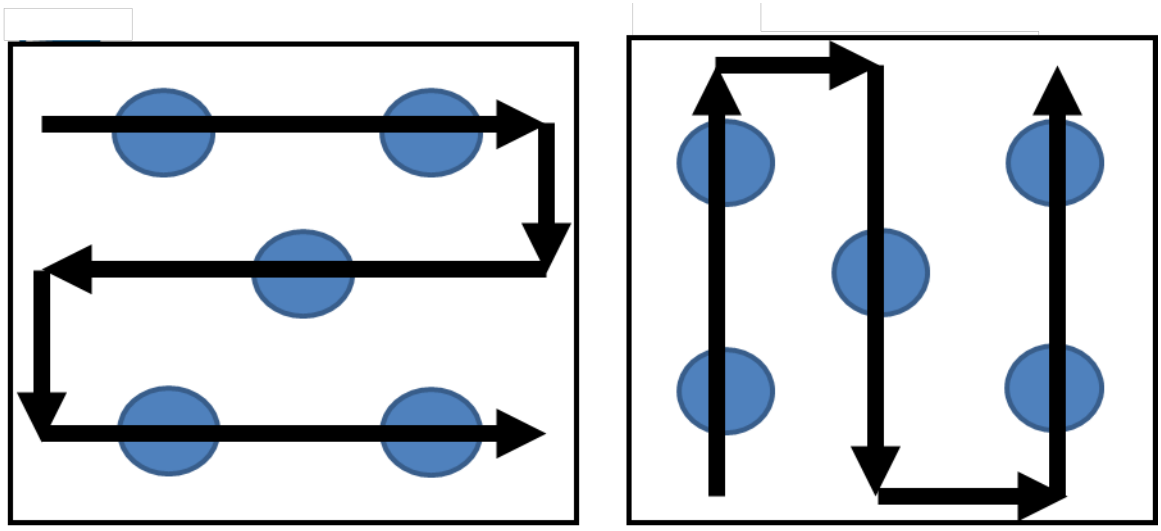

Figure A-7. Example of wiping pattern for each tested surface spiked with target analytes.

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