PPE Cleaning Validation

Verification of Cleaning, Decontamination, and Sanitization of Fire Fighter Garments

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SUPPLEMENT E: Report of Semi-Volatile Organic Chemical Contamination, Extraction, and Analysis Procedures

Crystal Forester
NIOSH NPPTL
Morgantown, West Virginia

August 2019

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Part 6 of 9

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Final Report by:

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(Part 6 of 9)

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Foreword

Fire fighter exposure to personal protective equipment (PPE) that is dirty, soiled, and contaminated is an increasing concern for long-term fire fighter health. Cancer and other diseases resulting from chronic exposures has become a leading issue and is presumed to be associated with fireground exposures relating to protection/hygiene practices and persistent harmful contamination found in fire fighter PPE.

While general cleaning procedures have been established in NFPA 1851, *Standard on Selection, Care, and Maintenance of Protective Ensembles for Structural Fire Fighting and Proximity Fire Fighting*, there are no requirements that demonstrate whether current cleaning practices will adequately remove contaminants from fire fighter PPE. Many manufacturer gear cleaning recommendations are vague and most cleaning product/process claims are unsubstantiated regarding contaminant removal effectiveness. Prior studies have identified persistent chemical and biological contaminants in structural firefighting PPE. Therefore, industry methodologies and practices are needed that can promote safe cleaning techniques so that fire fighters are not continually exposed to unclean or inadequately cleaned gear. It also important to set cleanliness criteria for the continued use of fire fighter protective clothing.

This project has established a relevant and credible procedure to validate "how clean is clean?" for fire service contaminated gear, and in doing so has addressed the primary goal of reducing fire fighter exposure to harmful contaminants in PPE. This includes the establishment of a repeatable and reproducible standardized method that can be used to determine the decontamination effectiveness of cleaning methods, and establish the needed fire service guidance for maintaining contaminant-free PPE as well as show that cleaning processes do not damage clothing. The project deliverables directly support efforts to update NFPA 1851 and other information that ensures consistent, effective cleaning processes of fire service gear.

This report is part six of a nine-part series on this topic of "PPE Cleaning Validation", with this part titled *"Supplement E: Report of Semi-Volatile Organic Chemical Contamination, Extraction, and Analysis Procedures"*. The following are all the reports in this series:

1. Master Report
2. Supplement A: Annotated Bibliography
3. Supplement B: Preliminary Work for Assessing PPE Cleaning Procedures
4. Supplement C: Investigation of Simulated Fire Ground Exposures
5. Supplement D: Evaluation of Outer Shell Liquid Retention Properties
6. Supplement E: Report of Semi-Volatile Organic Chemical Contamination, Extraction, and Analysis Procedures
7. Supplement F: Report of Heavy Metals Contamination, Extraction, and Analysis Procedures
8. Supplement G: Report of Biological Contamination, Extraction, and Analysis Procedures
9. Supplement H: Evaluation of Microbial Cleanliness of Selected ISP Advanced Cleaning Procedures

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Founded in 1896, NFPA is a global, nonprofit organization devoted to eliminating death, injury, property and economic loss due to fire, electrical and related hazards. The association delivers information and knowledge through more than 300 consensus codes and standards, research, training, education, outreach and advocacy; and by partnering with others who share an interest in furthering the NFPA mission. All NFPA codes and standards can be viewed online for free. NFPA's membership totals more than 65,000 individuals around the world.

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Report of Organic Chemical Contamination and Extraction Procedures

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Introduction

The purpose of this research was to develop procedures by which samples of outer shell fabric used in fire fighter protective clothing could be contaminated by known levels of selected semi-volatile organic compounds, subjected to cleaning, and then extracted and analyzed to determine residual concentrations of the same compounds. This methodology was intended to support procedures for evaluating the effectiveness of advanced cleaning procedures used for decontamination of fire fighter protective garments that had been exposed to products of combustion in structural fires. This research was carried out by investigating a variety of sample preparation techniques for contaminating clothing materials, applying industry practices for extracting these samples, and using gas chromatography with mass spectrometry (GC/MS). Significant analytical challenges were encountered for the simultaneous evaluation of three different classes of semi-volatile organic compounds as well as background chemicals found in the clothing outer shell fabric. This report provides a rationale for the specific choices made in setting up these procedures as well as testing that was conducted to validate the specific testing approaches applied within the project.

Selection of Standards

Several studies have investigated chemical contaminants found on turnout gear post fire. These studies have reported a variety of individual chemicals, several of which may be grouped in the following classes: polynuclear aromatic hydrocarbons (PAHs), phthalates, and phenolics.[1–7] Several chemicals in these classes are known carcinogens.[8] Due to the prevalence of these compounds in multiple studies and their deleterious health effects, chemicals from these three classes were chosen for a quantitative study. Other classes of chemical contaminants were considered such as perfluoroakyl substances and decabrominated diphenyl ethers but not pursued due to increased analytical technical challenges. Standards suitable for EPA Method 8270 that include the three selected semi-volatile organic compound (SVOC) classes were chosen in concentrations of 2000 μg/ml from two different suppliers. Table 1 contains a list of chemicals contained in each mixture, the respective CAS number, and estimated concentration. All dilutions and concentrations were calculated on the certified value provided with each lot received. For most of the work here, the PAH standard from the first supplier was used; however, due to availability issues, it was necessary to purchase a PAH standard containing the same individual chemicals plus three additional PAHs, at the same concentration from a second supplier. The standards were diluted in a 1:1 mixture of methylene chloride:benzene. Fresh dilutions were made at least weekly and all standards were stored in a refrigerator at 4° ± 2°C. All three classes of chemicals were combined to create a master standard from which dilutions were made.

Co-elution of peaks was an issue when choosing individual compounds for quantification. The co-elutions were not only from multiple chemicals within the master standard but also from the chemical finishes and other additives from the outer shell fabric that were removed during the extraction process. The chromatography and extraction solutions are discussed in a later section of this document.

Table 1: Analytes Contained in the Master Standard

Analyte	CAS #	Concentration (ug/l)		Analyte	CAS #	Concentration (ug/l)
Supplier 1				**Supplier 2**		
Acenaphthene	83-32-9	2000		1-Methylnaphthalene	90-12-0	2000
Acenaphthylene	208-96-8	2000		2-Methylnaphthalene	91-57-6	2000
Anthracene	120-12-7	2000		Acenaphthene	83-32-9	2000
Benzo (a) pyrene	50-32-8	2000		Acenaphthylene	208-96-8	2000
Benzo (b) fluoranthene	205-99-2	2000		Anthracene	120-12-7	2000
Benzo (g,h,i) perylene	191-24-2	2000		Benz (a) anthracene	56-55-3	2000
Benzo (k) fluoranthene	207-08-9	2000		Benzo (a) pyrene	50-32-8	2000
Benzo (a) anthracene	56-55-3	2000		Benzo (k) fluoranthene	207-08-9	2000
Chrysene	218-01-9	2000		Benzo (b) fluoranthene	205-99-2	2000
Dibenz (a,h) anthracene	53-70-3	2000		Benzo (g,h,i) perylene	191-24-2	2000
Fluoranthene	206-44-0	2000		Chrysene	218-01-9	2000
Fluorene	86-73-7	2000		Dibenz (a,h) anthracene	53-70-3	2000
Naphthalene	91-20-3	2000		Fluoranthene	206-44-0	2000
Phenanthrene	85-01-8	2000		Fluorene	86-73-7	2000
Pyrene	129-00-0	2000		Indeno (1,2,3-c,d) pyrene	193-39-5	2000
				Naphthalene	91-20-3	2000
				Phenanthrene	85-01-8	2000
				Pyrene	129-00-0	2000
Supplier 3 Phenolics				**Supplier 3 Phthalate Esters**		
2,3,4,6-Tetrachlorophenol	58-90-2	2000		bis (2-Ethylhexyl) phthalate	117-81-7	2000
2,4,5-Trichlorophenol	95-95-4	2000		Butyl benzyl phthalate	85-68-7	2000
2,4,6-Trichlorophenol	88-06-2	2000		Diethyl phthalate	84-66-2	2000
2,4-Dichlorophenol	120-83-2	2000		Dimethyl phthalate	131-11-3	2000
2,4-Dimethylphenol	105-67-9	2000		Di-n-butyl phthalate	84-74-2	2000
2,4-Dinitrophenol	51-28-5	2000		Di-n-octyl phthalate	117-84-0	2000
2,6-Dichlorophenol	87-65-0	2000				
2-Chlorophenol	95-57-8	2000				
2-Methyl-4,6-dinitrophenol	534-52-1	2000				
2-Methylphenol	95-48-7	2000				
2-Nitrophenol	88-75-5	2000				
3-Methylphenol*	108-39-4	1000				
4-Chloro-3-methylphenol	59-50-7	2000				
4-Methylphenol*	106-44-5	1000				
4-Nitrophenol	100-02-7	2000				
Dinoseb	88-85-7	2000				
Pentachlorophenol	87-86-5	2000				
Phenol	108-95-2	2000				
***coelute**						

Selection of Fabric

Two fire fighter protective clothing outer shell fabrics (Fabric A and Fabric B) were chosen for testing. Fabric A was a 7.5 oz/yd^2 ripstop fabric composed of 55% para-aramid, 37% PBI, and 8% liquid crystal polymer, multi-filament yarns. Fabric B is a 6.6 oz/yd^2 plain weave fabric composed of 60% para-aramid and 40% meta-aramid. Both fabrics have component recognition to the 2013 and 2018 editions of the NFPA 1971 standard.

Upon receipt of the bolt, samples of Fabric A were cut into five yard pieces and laundered five times with the following conditions in Table 2.

Table 2: Specimen Conditions

Temperature	105° F
Detergent	Detergent B
G-Force	<100 G
Drying	< 105° F

Swatches for testing were cut from the laundered pieces. Due to the finish that is applied to the fabric by the manufacturer, water-based solutions did not easily penetrate the fabric when the chemicals were applied, therefore all standards applied were in a solution of 1:1 methylene chloride:benzene. During the extraction procedure, the finish was removed from the swatch and some of its individual chemicals were discovered in the chromatograph after analysis. Some of these background peaks co-eluted with a few of the target semi-volatile organic compound peaks in the standards mixture.

Due to the difficulties of applying the chemicals to the Fabric A fabric and the interference of the chemicals from its durable water repellent (DWR) finish, a second fabric was evaluated for suitability for this project. Fabric B was received in a “scoured” condition from the manufacturer, where the fabric was treated in a hot alkaline solution to remove any finishes to allow as a precondition for the easier application of application of dyes to the fabric. The scoured Fabric B fabric did absorb all liquids applied to the surface including water, and in the absence of the DWR finish, the background peaks were reduced. However, during a visual inspection of the swatches after the laundering process, a significant amount of fraying was observed. Also, the percent removal of some of the individual chemicals was significantly higher than when using Fabric A. Because this fabric did not simulate real-world usage, it was determined that the project would proceed using only the Fabric A fabric.

Initially 6″ × 6″ swatches were used in this study; however, due to interferences observed in the chromatograms from the outer shell fabric coatings and finishes, the swatch size was reduced to a 3″ × 6″ swatch. This size provided sufficient surface area to apply the standards but reduced the amount of interferences in the chromatograms.

Contamination of Fabric

Several methods were attempted for applying chemicals to Fabric A. Initial experiments were conducted with methanol and either 100 mesh activated charcoal to simulate soot, or with the addition of a methyl orange-xylene cyanol indicating solution (MO-XC) (LabChem, Zelienople, PA) to visually assess the accuracy of the technique.

Airbrush Sprayer Technique

A single action airbrush shown in Figure 1 was modified to attach 4 ml glass vials containing 1 ml of chemical solution with ~5 mg activated charcoal using the heavy fluid tip. The 6″ × 6″ fabric swatch was placed between a square aluminum template with a spraying area of a 5″ × 5″ and a 6″ × 6″ piece of blotter paper. The sample swatch assembly was suspended vertically and the contents of the vial were sprayed to cover the swatch. Two additional ml of methanol were added to the vial and the contents sprayed onto the swatch to rinse any remaining chemicals from the vial. This method allowed for an even application of chemicals to the swatch; however, overspray resulted in penetration through the swatch to the blotter paper and soot was found on the aluminum template indicating that all of the sample solution was not applied directly to the fabric. For these reasons, this technique was deemed inadequate for this study.

Figure 1: Airbrush sprayer used for initial investigation of contamination application (photo courtesy of NPPTL)

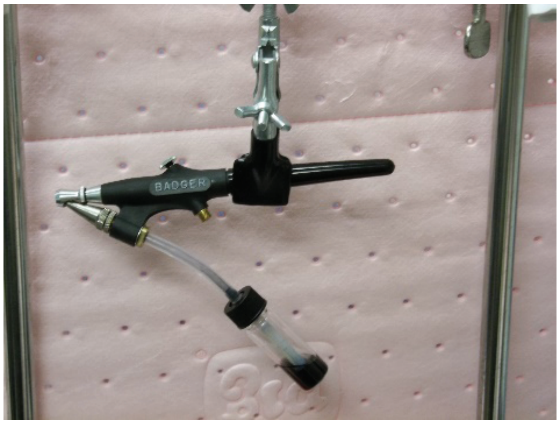
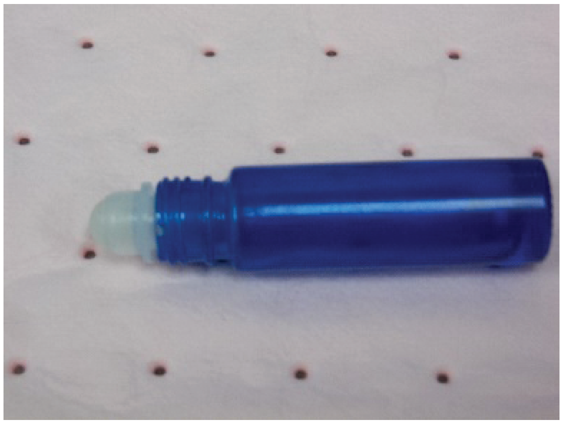


Figure 2: Rollerball applicator used as alternative contamination technique (photo courtesy of NPPTL)



Rollerball Applicator Technique

Methanol plus MO-XC indicating solution were pipetted into a glass bottle with a rollerball applicator (Figure 2). The solution was rolled onto swatches of fabric to determine if this application method could be accurately reproduced. The procedure required pressure to be placed on the applicator to allow the contents to flow. The pressure was high enough to cause the solution to penetrate the fabric and was visible on the blotter paper underneath. Also, a small amount of solution remained in the bottle that could not be removed. After two successive additions of methanol to the bottle, green liquid was still dispensed. For these reasons, this technique was deemed inadequate for the study.

Liquid Dripping from Small Bottle Technique

Methanol plus MO-XC indicating solution were pipetted into a plastic bottle with a dropper cap (see Figure 3). The solution was dripped sporadically across the fabric. Unfortunately, there was no way to control the droplet size and the solution frequently penetrated through the fabric onto the blotter paper. For this reason, this technique was deemed inadequate for the study.

Pipetting Technique

Methanol plus MO-XC indicating solution were pipetted onto fabric swatches using standard laboratory pipettes shown in Figure 4 with minimal penetration visible. Samples were analyzed using this method of coating fabrics, and the results in Table 3 showed acceptable reproducibility (±10% difference) for several of the compounds; however, a few compounds were outside these limits. One possible reason for these differences included the use of plastic pipette tips where chemicals could adhere to the inside of the tip. A second reason for the differences could have been that when the pipettes were used, it was difficult to control the flow from the tip. This resulted in either slow application of the chemicals, which allowed the solution to evaporate, or large drops on the fabric that could penetrate to the blotting paper. This was a viable method but took great control to prevent penetration through the fabric.

Figure 3: Small bottle used to drip contaminant liquids onto swatch (photo courtesy of NPPTL)

Figure 4: Pipettes used for applying contaminated solutions onto swatches (photo courtesy of NPPTL)

Table 3: Contamination Reproducibility Using Pipet

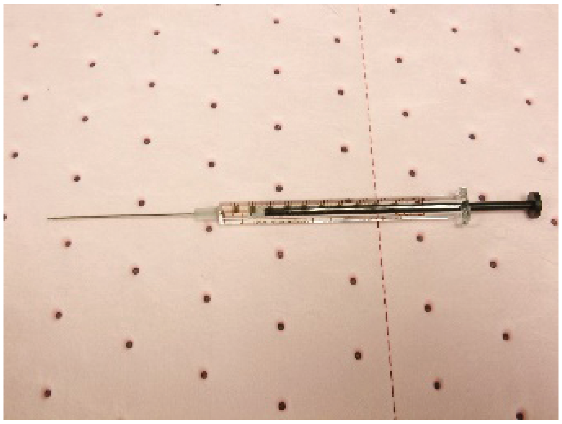
	Concentration ng/cm^2									
	Acenphthene	Diethyl phthalate	Fluorene	Phenanthrene	Anthracene	Di-n-octyl phthalate	Pyrene	Phenol	2-Nitrophenol	2,4,6-Trichlorophenol
Control 1	109	230	199	232	185	355	464	94	144	217
Control 2	108	270	222	230	218	338	293	76	134	214

Gas-tight Syringe Technique

After limited success with using a pipette to apply the standard solution to the fabric, it was determined a more precise and repeatable method was needed. Gastight syringes provided the accuracy and precision that are needed here with more control while dispensing the liquid. An example of a gas-tight syringe is shown in Figure 5.

To ensure complete dispensation of standard, the plunger was raised slightly to create an air pocket between the plunger and the liquid. The standard solution was then drawn into the Hamilton gastight syringe to the appropriate volume. The liquid was dispensed by slowly depressing the plunger and drawing the syringe tip across the fabric to lightly distribute the standard.

Figure 5: Example Gas-tight Syringe (photo courtesy of NPPTL)



Extraction

Several past studies have relied on extraction procedures described in EPA method 3500C.[9] Although several of these extraction procedures were developed to remove SVOCs from solid matrices, it was determined that none of these techniques alone were suitable for extracting contaminants from textiles due to the different chemicals that are applied during outer shell fabric finishing. The extraction procedure described below built on and also combined aspects of these procedures to extract contaminants from the subject textiles.

Solvents

Past studies have primarily used methylene chloride as the extraction solvent; however, EPA 3500C includes other solvents such as hexane, acetone, acetonitrile, and cyclohexane as secondary extraction fluids or rinses. In order to streamline the extraction process, a solvent mixture was developed for this extraction in the following ratios: 50% methylene chloride: 25% cyclohexane: 25% acetonitrile. The mixture was developed to extract multiple chemical classes simultaneously.

A mixture of 1:1 benzene:methylene chloride was used as the dilution solvent for the standards mixture. This mixture was typically made up by pipetting 1 ml each of PAH, phthalate, and phenol standards into an amber glass vial and diluting with 17 ml of the 1:1 benzene:methylene chloride mixture to make a 20 fold dilution of each of the standards. Aliquots of this mixture were used to coat the fabrics.

Extraction Procedure

Sample swatches were allowed to air dry after laundering and prior to extraction. Each dry 3″ × 6″ swatch was cut into 8 smaller squares and placed into a 300 ml PFA vessel. Five ¾″ diameter PTFE ball bearings and 50 ml of the solvent solution were added to the vessel. The vessel was capped tightly and placed on a laboratory shaker at approximately 230 rpm for 30 minutes. The ball bearings were added to the vessel to create friction to aid in the removal of the soils and chemicals from the fabrics. The vessels were removed from the shaker and placed in an ultrasonic water bath for 20 minutes with no heat. (NOTE: Even though the heating element was turned off, the temperature of the water in the water bath raised from room temperature to 40°–50°C from the operation of the bath for the 20-minute time.) At the end of the cycle the vessels were removed from the bath and the caps were loosened to prevent a vacuum forming within the vessel. The samples were allowed to rest until the temperature of the liquid inside the vessel returned to room temperature (approximately 10–15 minutes).

A 45 mm glass fiber filter (GFF) was placed on the fritted surface of the filtration apparatus, and the sample container was clamped to the flask as shown in Figure 6. This filtration apparatus was connected to the laboratory vacuum line. Sample from the extraction vessel was poured into the sample container and filtered through the GFF. The fabric squares were rinsed with an additional aliquot of solvent and squeezed and twisted to remove the excess solvent which was also filtered. The filtrate was transferred into a one hundred ml graduated oil tube for concentration of the extract solution.

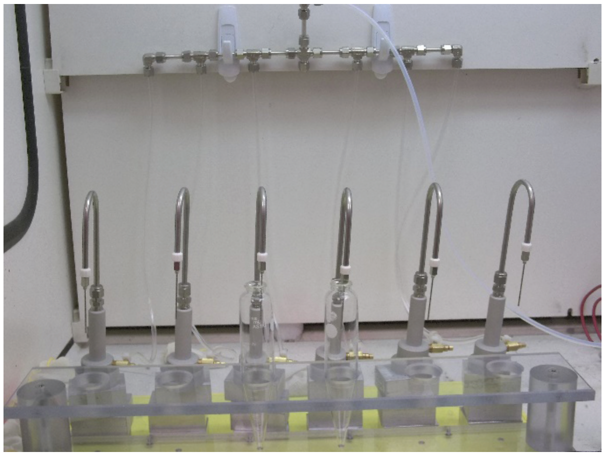
Figure 6: Filtration apparatus used in extraction of contaminated swatch (photo courtesy of NPPTL)

Sample Concentration and Clean-up

Sample Concentration

After transferring the filtrate to the oil tube, the tube was placed in a rack designed to hold the tube during the condensation procedure (Figure 7). These graduated conical tubes were ideal for concentrating samples given their taper lower shape and graduations for indication volumetric amounts. A mini-evaporator was connected to an ultra-high purity (UHP) nitrogen tank via an in-house built manifold that allowed for simultaneous concentration of six samples. The nitrogen stream was adjusted to prevent splashing, and the samples were gently condensed to ≤ 2.0 ml.

Figure 7: Custom-built evaporator for concentrating extraction samples (photo courtesy of NPPTL)

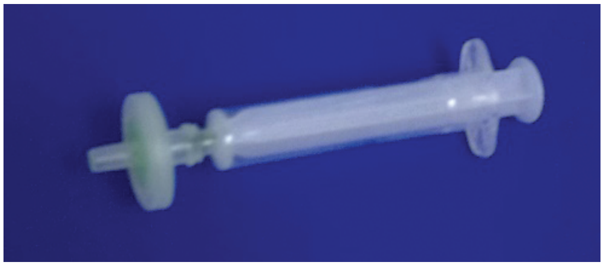


Sample Clean-up

After condensation, the tubes were removed from the rack and vortexed for 10–15 seconds to reincorporate solids dried on the sides of the tubes. Volumes of the liquid were measured by drawing the sample into a glass serological pipet. The liquid was returned to the tube and an aliquot of the solvent mixture was added to the tube so the final volume was 2.0 ml. The sample was placed on the vortex again; then the sample was transferred to a 10 ml beaker.

The sample was drawn into a 3 ml syringe, and a Polyvinylidene fluoride (PVDF) 0.45 µm syringe filter was placed on the end of the syringe (see Figure 8). The samples were filtered directly into pre-labeled 2.0 ml auto sampler vials for analysis.

Figure 8: Syringe with filter used for injection into sampler vials (photo courtesy of NPPTL)

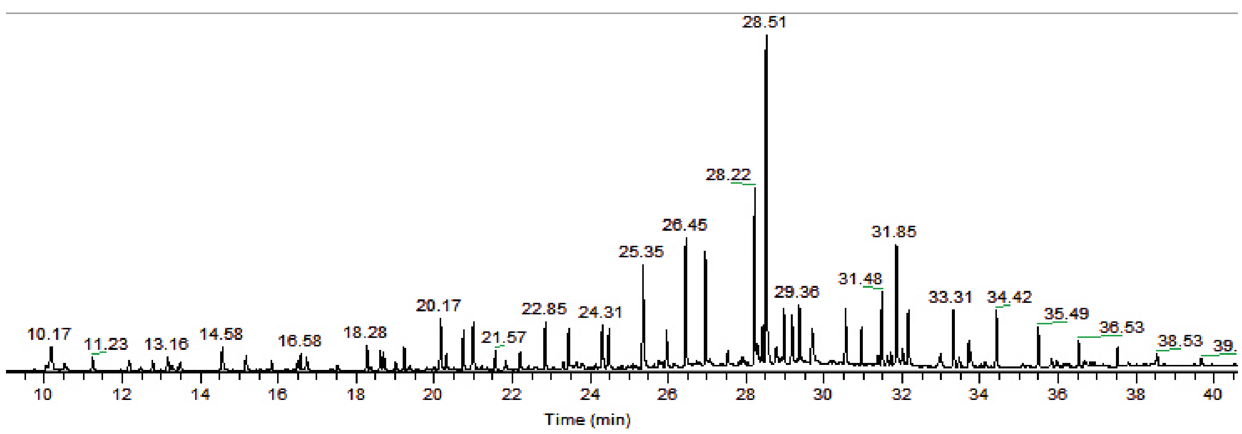


Sample Analysis and Data Processing

All samples were analyzed on a gas-chromatograph connected to a triple quadrupole mass spectrometer (GC/MS/MS). One microliter of sample was injected via an 8-position autosampler into a 200°C inlet containing a split/splitless straight with wool-based GC inlet liner. A fused silica nonpolar 30 m, 0.25 mm ID, 0.50 µm mass spectroscopy column with a guard column that has been deactivated but not coated with stationary phase was used to achieve separation. The oven temperature was held at 60°C for 2 minutes after injection; then the temperature was ramped at a rate of 7°C per minute until 310°C with a 10-minute hold. The temperature of the transfer line and ion source were 300°C.

Data was integrated using Excalibur software when possible. In the event of interference or over-lapping peaks, the peaks were manually integrated. Figure 9 provides an example chromatograph for the analysis of a contaminated specimen.

Figure 9: Chromatogram of extract from laboratory contaminated swatch

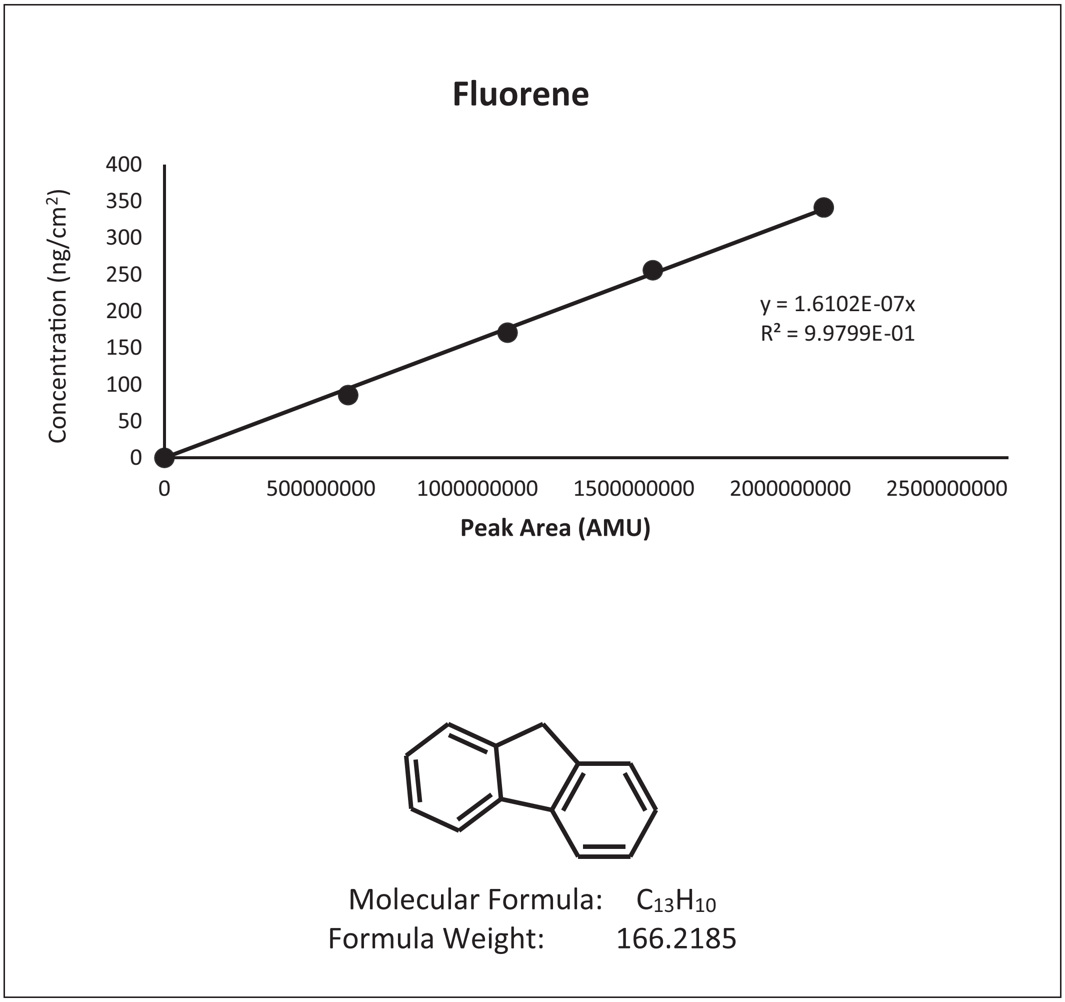


Calibration curves were developed for each analyte of interest by plotting the known concentrations (y-axis) vs the peak area (x-axis). All curves were forced through zero. To calculate the concentration of the contaminants, the slope of the calibration curve was used. The equation used for the calculation is the equation for the line: $y = mx+b$. As all calibration curves were forced through zero, the equation becomes $y = mx$ where y is the unknown concentration, m is the slope of the line, and x is the peak area of the contaminant. The following plot of fluorene is representative of all calibration plots (Figure 10).

A laboratory control sample was contaminated with the SVOC standard solution at the same time each set of swatches for laundering were contaminated. This control was extracted with the samples after they were returned to the laboratory. The concentration on these control samples was used as the initial concentration in calculating the percent removal. Percent removal (*%R*) was calculated using the following formula:

$$\%R = 100 \times \frac{([\text{Control}] - [\text{Swatch}])}{[\text{Control}]}$$

Figure 10: Fluorine calibration plot



Molecular Formula: $C_{13}H_{10}$
Formula Weight: 166.2185

Results

Laundry Study

Table 4 shows the % removal of contaminants in the initial laundry studies. Samples identified as Pant 1, Coat 1, or Trip blanks were actual blanks, which accounts for the high percent removal (>99). Unless otherwise specified, all samples were laundered using a water temperature of 105°C.

The data seen in Table 4 are the results from a study to compare analysis of the laundry kit, including the contaminated and uncontaminated samples at independent services providers (ISPs). The swatches in these studies were contaminated with PAH and phthalate standards only. Results of >99 percent indicate that the individual compound was not detected during analysis.

Table 4: Results from ISP Study

		Acenphthene	Diethyl phthalate	Fluorene	Phenanthrene	Anthracene	Di-n-octyl phthalate	Pyrene
ISP 1	Pant 1	>99	>99	>99	>99	>99	>99	>99
	Pant 2	22	86	27	21	6	34	31
	Pant 3	52	85	44	26	13	28	28
	Coat 1	>99	>99	>99	>99	>99	>99	>99
	Coat 2	61	91	48	30	16	37	34
	Coat 3	39	86	35	28	14	29	33
ISP 1	Pant 1	>99	>99	>99	>99	>99	>99	>99
	Pant 2	55	93	58	53	39	55	62
	Pant 3	56	93	61	54	40	50	52
	Coat 1	>99	>99	>99	>99	>99	>99	>99
	Coat 2	46	94	55	53	37	49	55
	Coat 3	33	92	41	47	31	43	50
ISP 1	Pant 1	>99	>99	>99	>99	>99	>99	>99
Wash temp	Pant 2	73	96	74	61	46	40	40
140°C	Pant 3	68	95	67	57	41	34	39
	Coat 1	>99	96	>99	>99	>99	>99	>99
	Coat 2	67	95	68	62	47	49	50
	Coat 3	61	>99	67	63	49	41	38
ISP 2	Trip Blank	>99	>99	>99	>99	>99	>99	>99
	Pant 1	>99	>99	>99	>99	>99	>99	>99
	Pant 2	76	95	73	53	51	55	49
	Pant 3	79	96	76	59	57	60	55
	Coat 1	>99	>99	>99	>99	>99	>99	>99
	Coat 2	67	95	60	49	36	50	46
	Coat 3	75	95	71	49	42	47	23
ISP 3	Trip Blank	>99	>99	>99	>99	>99	>99	>99
	Pant 1	>99	>99	>99	>99	>99	>99	>99
	Pant 2	19	82	23	46	29	48	42
	Pant 3	31	88	40	58	44	56	54
	Coat 1	>99	>99	>99	>99	>99	>99	>99
	Coat 2	22	80	21	48	30	39	29
	Coat 3	11	84	23	47	29	43	34

Table 5 contains the results of additional ISP testing after phenols were added into the mixture of compounds.

Table 5: Additional ISP Testing with the Inclusion of Phenols

	Sample ID	Phenol	2-Nitrophenol	2,4,6 Trichlorophenol	Acenphthene	Diethyl phthalate	Fluorene	Phenanthrene	Anthracene	Di-n-octyl phthalate	Pyrene
ISP 1	Coat 1	>99	>99	>99	>99	>99	>99	>99	>99	49	>99
Wash temp	Coat 2	>99	>99	97	81	95	67	57	38	40	60
160°C	Coat 3	>99	>99	96	82	95	63	60	43	45	62
	Pant 1	>99	>99	>99	>99	>99	>99	>99	>99	91	>99
	Pant 2	>99	>99	>99	79	96	64	58	40	48	66
	Pant 3	>99	>99	96	78	96	62	58	39	58	64
ISP 2	Coat 1	>99	>99	>99	>99	>99	>99	>99	>99	93	>99
	Coat 2	>99	>99	89	96	97	78	74	70	60	68
	Coat 3	>99	>99	92	89	95	99	56	48	60	66
	Pant 1	>99	>99	>99	>99	>99	>99	>99	>99	95	>99
	Pant 2	>99	>99	88	93	96	99	53	43	65	72
	Pant 3	>99	>99	88	96	95	99	50	39	70	72
ISP 1	Coat A1	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99
	Coat A2	>99	>99	96	99	96	68	34	56	28	29
	Coat A3	>99	>99	95	62	94	41	27	56	67	50
	Pant A1	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99
	Pant A2	>99	>99	97	82	95	60	40	55	56	50
	Pant A3	>99	>99	95	71	93	41	20	49	39	36
	Coat B1	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99
	Coat B2	>99	>99	98	82	96	59	39	74	37	52
	Coat B3	>99	>99	97	69	93	38	27	61	20	36
	Pant B1	>99	>99	>99	>99	>99	>99	>99	>99	>99	100
	Pant B2	>99	>99	97	83	96	67	56	70	61	64
	Pant B3	>99	>99	96	83	94	61	45	68	10	72
	Coat C1	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99
	Coat C2	>99	>99	97	83	96	64	50	50	68	46
	Coat C3	>99	>99	96	83	94	61	45	46	42	36
	Pant C1	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99
	Pant C2	>99	>99	97	85	96	65	52	53	4	41
	Pant C3	>99	>99	97	83	97	68	57	58	43	56
ISP 2	Coat A1	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99
	Coat A2	>99	>99	97	98	100	92	66	69	43	55
	Coat A3	>99	>99	97	97	98	85	66	68	18	77
	Pant A1	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99
	Pant A2	>99	>99	97	97	96	70	64	79	37	54
	Pant A3	>99	>99	98	97	98	85	67	68	17	77
	Coat B1	>99	>99	97	95	98	83	>99	>99	>99	>99
	Coat B2	>99	>99	96	95	97	77	96	64	43	57

	Sample ID	Phenol	2-Nitrophenol	2,4,6 Trichlorophenol	Acenphthene	Diethyl phthalate	Fluorene	Phenanthrene	Anthracene	Di-n-octyl phthalate	Pyrene
	Coat B3	>99	>99	97	93	97	78	69	69	58	61
	Pant B1	>99	>99	>99	99	98	94	98	97	>99	93
	Pant B2	>99	>99	97	94	97	80	64	65	68	64
	Pant B3	>99	>99	98	95	97	83	70	73	63	68
	Coat C2	>99	>99	90	96	97	83	69	68	59	64
	Coat C3	>99	>99	96	96	97	84	73	43	30	81
	Pant C1	>99	>99	>99	>99	>99	>99	>99	>99	>99	>99
	Pant C2	>99	>99	96	83	94	62	55	54	17	42
	Pant C3	>99	>99	96	94	97	80	70	68	52	59

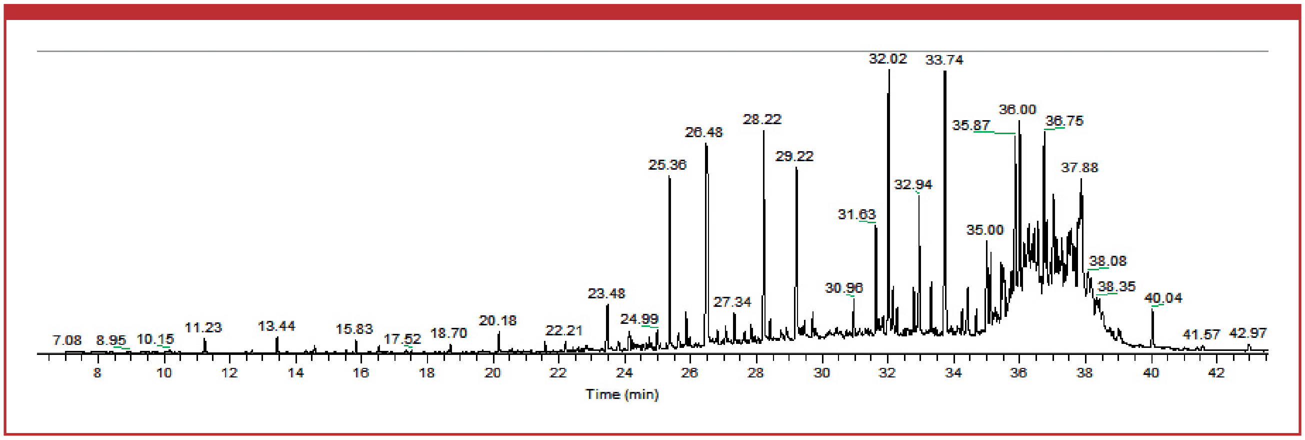
Evaluation of Field-Soiled Gear

In order to assess the viability of the laboratory-contaminated samples being used for determining decontamination effectiveness, comparative research testing was carried out on field-soiled (contaminated) clothing. Four sets of gear that had been recently worn at a fire scene were received at the NIOSH Morgantown facility for this project. The gear was placed in PTFE bags and then sealed to prevent off-gassing. The gear remained in this state until analysis.

Swatches were cut from areas of the garments that were visibly soiled. The swatches were split into groups for direct extraction or laundering. The samples that were directly extracted were analyzed, and compounds from several classes of chemicals were identified. As the number of individual chemicals found on the gear was extremely high, it was not possible to purchase standards for each chemical. Also, sample interference prevented positive identification between similar compounds; however, the classes of chemicals that these belonged to included alkanes, alkenes, carboxylic acids, phenols, phthalates, PAHs, isocyanates, phosphates, alcohols, esters, amides ethers, and other organic acids.

Attempts were made to spike swatches of the contaminated gear with the standard mixture, directly extract one swatch, and launder and extract the second swatch. Unfortunately, with the amount of contamination already on the fabric, the results could not be interpreted due to significant interferences and a large mass of unresolved compounds in the chromatograph. Figure 11 is a representative chromatograph of a swatch removed from one of the contaminated gear items.

Figure 11: Chromatogram of extract from field-soiled swatch



One contaminant, di-isooctyl phthalate, was found on several swatches of the field-soiled gear. The peaks were integrated prior to and after laundering and the results are shown in Table 6. These data were for demonstration purposes only as the peak areas greatly exceeded the calibration range of the instrument. Also, the assumption was made that the chemical contamination was uniform across the garment. Duplicate samples from each garment were averaged for both the soiled and laundered swatches.

Table 6: Field-Soiled Gear Cleaning Efficiency

	Soiled Average ng/cm^2	Laundered Average ng/cm^2	Percent Removal %
Garment 1	3431	1022	70
Garment 2	3767	2434	35
Garment 3	4360	2468	43
Garment 4	3961	1888	52
Garment 5	3535	2102	41
Garment 6	3634	1943	47
Garment 7	3154	2439	23
Garment 8	3923	2772	29

Discussion

Cleaning or decontamination efficiency is reported as the percentage of the chemical removed. All of the chemicals studied had a wide removal range. A partial explanation for this could be the length of time between the chemical contamination of the outer shell fabric swatch and the actual extraction. The swatches were shipped overnight to and from the ISPs; however, the actual arrival times were not always the next day. Also, depending on the work load at the ISP, the samples were not always laundered on the day they were received. Table 7 contains average percent removals from data in Table 4 with the blanks excluded.

Table 7: Average Percent Removals

	Phenol	2-Nitrophenol	2,4,6 Trichlorophenol	Acenphthene	Diethyl phthalate	Fluorene	Phenanthrene	Anthracene	Di-n-octyl phthalate	Pyrene
Average	>99	>99	96	87	96	60	56	57	47	58

These data show that the cleaning efficiency was greater for the lower molecular weight compounds of higher volatility as expected. Consequently, specific strategies and methods should be developed to enhance the removal of these SVOCs to prevent dermal contact during future usage of the garments.

Field-Soiled Gear

Several contaminants were found on the field-soiled gear. The only information that was supplied to the laboratory was the fire fighter gear was recently used at the scene of a fire event. Compounds in many of the classes could have been present as a result of the fire or from other sources. For example, phosphates are used in detergents and fertilizers, phthalates are in personal care products and plastics, etc. It is impossible to determine the actual source of the contamination. Di-n-octyl phthalate was found in all of the soiled samples. The average percent removal was 42% which is only 5% lower than the samples in the ISP study even with the concentrations on the swatches being outside the linear calibration range.

Many of the contaminants in the field-soiled gear were unidentifiable due to interferences. Also, in each chromatograph a large "hump" signifying unresolved masses was present. These humps appear when the analytes in the tested specimen are not compatible with the stationary phase of the GC column. Additional analyses would be needed with a column with a stationary phase such as carbowax to resolve this issue. However, the principal purpose of this research was to focus on specific techniques applicable to the target classes of SVOC selected for this study.

Conclusions

The objectives of this study were met. Viable, reproducible methods were developed to contaminate fire fighter protective clothing outer shell swatches with selected SVOCs, extract the analytes from these swatches, clean the sample filtrate, and to provide a reliable analysis of the filtrate. These methods provide the basis for laboratory analysis and verification of advanced cleaning practices of ISPs and other organizations for the cleaning of fire fighter gear exposed to products of combustion.

Additional work should be completed to determine ways to increase the percent removal for the larger molecular semi-volatile compounds that are persistent in outer shell fabrics.

Bibliography

1. Alexander, B. M.; Baxter, C. S., Plasticizer contamination of firefighter personal protective clothing—A potential factor in increased health risks in firefighters. *Journal of Occupational and Environmental Hygiene* **2014,** *11* (5), D43–D48.10.1080/15459624.2013.877142
2. Baxter, C. S.; Hoffman, J. D.; Knipp, M. J.; Reponen, T.; Haynes, E. N., Exposure of firefighters to particulates and polycyclic aromatic hydrocarbons. *Journal of Occupational and Environmental Hygiene* **2014,** *11* (7), D85–D91.10.1080/15459624.2014.890286
3. Brandt-Rauf, P. W.; Fallon Jr, L. F.; Tarantini, T.; Idema, C.; Andrews, L., Health hazards of fire fighters: Exposure assessment. *British Journal of Industrial Medicine* **1988,** *45* (9), 606–612.
4. Caux, C.; O'Brien, C.; Viau, C., Determination of firefighter exposure to polycyclic aromatic hydrocarbons and benzene during fire fighting using measurement of biological indicators. *Applied Occupational and Environmental Hygiene* **2002,** *17* (5), 379–386.10.1080/10473220252864987
5. Fabian, T. Z.; Borgerson, J. L.; Gandhi, P. D.; Baxter, C. S.; Ross, C. S.; Lockey, J. E.; Dalton, J. M., Characterization of Firefighter Smoke Exposure. *Fire Technology* **2014,** *50* (4), 993–1019.10.1007/s10694-011-0212-2
6. Fent, K. W.; Evans, D. E.; Booher, D.; Pleil, J. D.; Stiegel, M. A.; Horn, G. P.; Dalton, J., Volatile Organic Compounds Off-gassing from Firefighters' Personal Protective Equipment Ensembles after Use. *J Occup Environ Hyg* **2015,** *12* (6), 404–14.10.1080/15459624.2015.1025135
7. Feunekes, F. D.; Jongeneelen, F. H.; van Laan, H.; Schoonhof, F. H., Uptake of Polycyclic Aromatic Hydrocarbons Among Trainers in a Fire-Fighting Training Facility. *American Industrial Hygiene Association Journal* **1997,** *58* (1), 23–28
8. IARC, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, List of Classifications, Volumes 1–117. Cancer, I. f. R. o., Ed.
9. EPA, U., SW 846 METHOD 3500C ORGANIC EXTRACTION AND SAMPLE PREPARATION. Agency, U. E. P., Ed. 2007.

Appendix A: Organic Analysis—Supplemental Information; Materials and Methods

Equipment

Gas chromatograph/mass spectrometer
A fused silica nonpolar 30 m, 0.25 mm ID, 0.50 µm mass spectroscopy column with a guard column that has been deactivated but not coated with stationary phase (or equivalent)
Laboratory oven (for drying miscellaneous supplies and glassware)
Platform shaker
Ultrasonic bath
Mini-evaporator concentrator
Various Eppendorf or other pipettes
Gastight syringes

Glassware/PFAware

300 ml PFA jars with lids
100 ml oil tubes
Glass filtration flask assembly
Various beakers
Racks to hold oil tubes
⅝ or ¾″ PTFE bearing balls
Glass funnels

Lab supplies

Assorted vials
Disposable glass pipettes
Disposable pipette tips
47 mm glass fiber filters
45 µm PVDF syringe filters
3 ml syringes
Appropriate gloves for acetonitrile

Chemicals

PAH standards
Phthalate standards
Phenolics standards
Methanol
Benzene
Methylene chloride
Acetonitrile
Cyclohexane
UHP nitrogen

Calibration Curves

1. Apply known concentrations to swatches and extract and analyze following sample procedure
2. Integrate and plot concentration vs. peak area for each compound

Contamination of Swatch

1. Mix standards in concentration you want to apply
2. Withdraw the appropriate volume into a gas-tight syringe
3. Gently dispense the standard onto the swatch

Extractions Preparation

1. Thoroughly clean, rinse, and dry all glassware and PFAware
2. Mix extraction solvent: 50% methylene chloride, 25% acetonitrile, 25% cyclohexane
3. Mix PAH/phthalate dilution solution: 1:1 Benzene:methylene chloride

Extraction

1. Cut laundered swatch into smaller pieces (8 small pieces work well) and place in PFA jar
2. Add 5 PTFE bearing balls
3. Add 50 ml extraction solvent (step 2 above)
4. Place sample vessel(s) on platform shaker at 230 ± 10 rpm and shake for 30 minutes
5. Remove vessel(s) from platform shaker and place in ultrasonic cleaner bath for 20 minutes, no heat. The temperature may increase due to normal operation of the equipment (~40–50°C range)
6. Vent vessels immediately after the ultrasonic cleaner shuts off as the temperature increase will cause a vacuum
7. Filter samples through glass vacuum filtration using GFF filters
8. Rinse vessel and cloth pieces with a small amount of extraction solvent
9. Squeeze any excess solvent from the cloth pieces into the filtration flask
10. Transfer contents from filter flask to oil tube using small glass funnel

Clean-up

1. Place oil tube in rack under mini-vap connected to UHP nitrogen and evaporate contents to ~2 ml (Volume must be 2 ml or below but not dry)
2. Vortex tube with evaporated contents to incorporate any solids dried on side of tube
3. Measure contents of tube with disposable sterile pipet and record volume
4. Return contents to oil tube and add the appropriate amount of solvent to increase the final volume to 2 ml
5. Vortex tube and remove contents with disposable glass pipet into small (10 ml) glass beaker
6. Remove the contents from the beaker via 3 ml syringe and attach 2μm syringe filter
7. Filter sample into auto-sampler vial

Analysis

1. Analyze via GC/MS using the following conditions
   a. Inlet temp: 200°C
   b. Transfer line temp: 300°C
   c. Ion source temp: 300°C
   d. Oven temp: 60°C—hold two minutes
   e. Ramp: 7° per minute to 310°C—hold 10 minutes
2. Integrate and calculate concentration remaining and % removal based on calibration curves