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Effects of Temperature and Advanced Cleaning Practices on the Removal of Select Organic Chemicals from Structural Firefighter Gear

Crystal D. Forester * *and Jay Tarley, Evaluation and Testing Branch, National Personal Protective Technology Laboratory, National Institute for Occupational Safety and Health, 1000 Frederick Lane, Morgantown, WV 26508, USA*

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Abstract. There are approximately 1.2 million firefighters in the United States. In addition to fighting fires, they also participate in various tasks including emergency rescues, providing emergency medical care, driving, operating and maintaining fire vehicles and other apparatuses and continued training. During the course of their duties, firefighters are often exposed to carcinogenic chemicals that may accumulate on their turnout clothing. To determine if these chemicals can be removed and to measure the efficacy of current cleaning protocols, a study was developed to assess these protocols which call for a maximum water temperature of 105°F and no solvents. The results showed that volatile and small semi-volatile chemicals such as dimethyl phthalate and chlorinated phenols had cleaning efficiencies of 85% or greater. However, for polycyclic aromatic hydrocarbons (PAHs), the cleaning efficiency was only 20% to 50%. To determine if it is possible to remove the more persistent PAHs, temperatures were increased to 125°F and 140°F, and a respective increase in cleaning efficiencies of the PAHs was seen. The protocols were then adapted to add a pre-soak cycle which, when combined with the increased temperatures, resulted in an increase of the PAH cleaning efficiency range from 50 to 80%, compound dependent. This work provides a starting point for discussions between the National Fire Protection Association (NFPA) and other standards organization and manufacturers to determine if increased temperatures and chemical soaks would be detrimental to gear as they are currently not advised.

Keywords: Firefighter, Laundry, PAH, Phthalates

1. Introduction

Cancer is the second leading cause of death in the United States [1]. A 2016 study by National Institute for Occupational Safety and Health (NIOSH) found that firefighters suffer from a higher risk of certain cancers than the general population

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*Correspondence should be addressed to: Crystal D. Forester, E-mail: ckf7@cdc.gov including digestive, oral, respiratory, urinary cancers, and mesothelioma [2, 3]. Cancer is one of the leading causes of firefighter fatalities and is presumed to be associated with fireground exposures as it relates to protection/hygiene practices and persistent harmful contamination found in personal protective equipment (PPE) clothing. Inhalation exposures from incidents that produce airborne contaminants have been addressed throughout the years with respiratory protection and administrative controls on the fireground, at vehicle fires, and during overhaul as examples [4]. When firefighters exit the active fire area, it is assumed they are safe from airborne contaminants due to the PPE they are wearing. However, recent literature shows a rise in occupational cancer among firefighters [5]. A possible reason for this could be inhalation and/or dermal exposures after the fire event [6] and the re-use of improperly cleaned turnout gear. Respiratory protection (e.g. Self-Contained Breathing Apparatus (SCBA)) protects the firefighters from hazardous contaminants during firefighting operations; however, the turnout gear worn by firefighters has the potential to store these contaminants. These contaminants can then be inhaled or absorbed through the skin by the wearers of the contaminated turnout gear [3].

Several studies have been published showing that firefighters can be exposed to many hazardous chemicals and contaminants from structure fires such as carbon monoxide, nitrogen dioxide, hydrogen chloride, hydrogen cyanide, sulfur dioxide, acrolein, formaldehyde, acetaldehyde, benzene, as well as materials in fire debris such as asbestos from older structures [7–11]. In addition, there have also been several studies suggesting that cancer and other diseases resulting from chronic exposures are a leading concern and presumed to be associated with fireground exposures persistent harmful contamination found in firefighter PPE [12]. A recent landmark study by NIOSH and collaborators indicates that firefighters have higher rates of cancers in respiratory, digestive and urinary systems than the general population [13]. Additional studies have identified fireground contaminants persistent in structural firefighting PPE. One such study, “Firefighter Exposure to Smoke Particulates” by Fabian, et al., reported contaminant levels in firefighter protective hoods and gloves after actual fires [14]. A related study examined a variety of different types of contaminants on turnout clothing samples taken from one department. This provided a cursory analysis of the potential exposure levels of these chemicals. This study found concentrations of several PAH and phthalate compounds on turnout gear with concentrations greater than 1000 μg of contaminant/kg of fabric [15].

Other studies have been conducted to understand how firefighter protective clothing becomes contaminated through its use on the fireground [16–18]. It is generally accepted that textile materials retain chemicals which are less volatile but considerably more dangerous such as known carcinogens including PAHs, and are less likely to be removed by general cleaning procedures [19, 20]. Furthermore, many of these chemicals not only contaminate clothing, but may penetrate through textile layers or through interface areas, to contact skin. Schneider et al. developed a model to predict dermal exposure and uptake through clothing [21] Morrison, et al. demonstrated that contaminated clothing showed an increased dermal uptake of diethyl phthalate and di-n-butylphthalate when compared to clean clothing [22]. A recent study by Fent, et al., showed dermal absorption of PAHs and benzene during training exercises in full ensemble [23]. Also, recent studies have indicated that skin in the neck/head area of firefighters is the portion of their bodies that are most likely to become contaminated with fireground soot and chemicals [12, 24–26]. Modern residential fires present new exposure hazards such as plasticizers (phthalate diesters) which may contribute to the increased risk of cardiovascular disease and cancer in firefighters [27]. Research by NIOSH has shown that firefighters are not only exposed to toxic chemicals while at the fireground but also after extinguishment due to the off-gassing from the scene and from the PPE worn while fighting the fire [28, 29].

Semi-volatile organic compounds (SVOCs) are a sub-class of volatile organic compounds (VOCs) that have higher molecular weights and boiling points (220 °C–400 °C) than VOCs. Due to the high boiling points, SVOCs are able to partially partition into the gas-phase and adhere to surfaces [30]. SVOCs are ubiquitous in indoor environments as they are used as coatings and finishes, plasticizers or in personal care products [30, 31]. Because of the abundance of these compounds in built environments and modern furnishings, firefighters are exposed to these chemicals during firefighting operations. There are multiple health effects associated with this class of chemicals including asthma, allergies, low birth weight, reproductive issues, and cancer. Several SVOCs are known endocrine disruptors that can alter natural hormone pathways leading to reproductive or developmental processes that could lead to obesity, diabetes, infertility, attention deficit disorder and cancer [32–34]. Xu summarized these and multiple other health effects related to SVOCs in 2011 [35]. Additionally, in 2022, IARC changed its classification of the occupation of firefighting from group 2B (possible human carcinogen) to group 1, (human carcinogen) [12].

The objective of the research here is to evaluate NFPA cleaning guidance using a water temperature of 105°F and compare the cleaning efficiencies of multiple compounds with results from laundering at elevated temperatures and using a solvent-based degreaser in a pre-soak step. These results will provide valuable information to firefighter standards committees, including NFPA, and to gear manufacturers regarding advancements in cleaning practices.

2. Materials and Methods

General cleaning guidelines for firefighter turnout gear were initially established by NFPA 1500, Standard for a Fire Department Occupational Safety, Health, and Wellness Program. These requirements are described in NFPA 1851, *Standard on Selection, Care, and Maintenance of Protective Ensembles for Structural Fire Fighting and Proximity Fire Fighting*. In this work, the current guidelines were evaluated to determine if the maximum recommended temperature was sufficient to remove SVOCs. Also, additional steps were added to the programmable extractor to perform an agitated soak cycle to determine if a pre-soak would increase cleaning efficiencies of a variety of SVOCs.

Fabric swatches were prepared and analyzed using methods previously published on the Fire Protection Resource Foundation (FPRF) webpage [36]. A brief description follows below.

2.1. Fabric and Standards

A firefighter protective clothing outer shell material consisting of a modified plain weave of PBI®/DuPont™ Kevlar® with a Super Shelltite™ finish was used for all of the analyses here. Swatches (7.6 cm × 15.2 cm) were cut from new (unlaundered) cloth. Due to the durable water repellent finish (DWR) 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. Chemical standards of polyaromatic hydrocarbons (PAHs), phthalates and phenols were purchased from MilliporeSigma (Burlington, MA) and Restek (Bellefonte, PA) in a concentration of 2000 μg/L and combined into one mixture (Table 1). The desired end concentration of each analyte was calculated then the appropriate volume of its standard was added to a volumetric flask. This was repeated for each standard into the same volumetric then the mixture was diluted to volume with a solution of 1:1 methylene chloride:benzene. The chemicals that were quantified in this study were chosen because they have either been found on contaminated firefighter gear in previous studies, have known health effects and did not have interferences with background chemicals in the chromatography.

2.2. Sample Preparation

Standards were diluted and applied to the surface of the swatch using a Hamilton (Reno, NV) gas tight syringe. To ensure complete dispensation of the 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 gas tight syringe to the appropriate volume depending on the concentration required. The liquid was dispensed by slowly depressing the plunger and drawing the syringe tip across the fabric to lightly distribute the standard across the entire swatch. The swatches were allowed to air dry for approximately 20 s then were placed between aluminum foil sheets and stored in a refrigerator until laundered. Typically, sample swatches would be spiked with an isotope labelled standard, however, there were considerable chromatographic interferences between the analytes and the background chemicals in these samples. It was decided to prepare, extract and analyze the calibration curves and control and check standard samples in the same manner as the samples. The only difference was the calibration, control and check standard swatches were not laundered. Control swatches were also coated with the same concentrations of analytes and extracted without laundering. The concentration of individual chemicals applied to each swatch ranged from 345 to 348 ng/cm^2. Controls were analyzed to ensure the calibration curves remained valid throughout the experimental runs. These control swatches were prepared at the same time as the swatches to be laundered but stored in the refrigerator in aluminum foil until the laundered swatches were ready to be extracted. The control

Table 1
Multi-Component Combined Standard

Analyte	CAS #	Concentration (ug/l)
1-Methylnaphthalene	90–12–0	2000
2-Methylnaphthalene	91–57–6	2000
Acenaphthene	83–32–9	2000
Acenaphthylene	208–96–8	2000
Anthracene	120–12–7	2000
Benz(a)anthracene	56–55–3	2000
Benzo(a)pyrene	50–32–8	2000
Benzo(k)fluoranthene	207–08–9	2000
Benzo(b)fluoranthene	205–99–2	2000
Benzo(g,h,i)perylene	191–24–2	2000
Chrysene	218–01–9	2000
Dibenz(a,h)anthracene	53–70–3	2000
Fluoranthene	206–44–0	2000
Fluorene	86–73–7	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
2,3,4,6-Tetrachlorophenol	58–90–2	2000
2,4,5-Trichlorophenol	95–95–4	2000
2,4,6-Trichlorophenol	88–06–2	2000
2,4-Dichlorophenol	120–83–2	2000
2,4-Dimethylphenol	105–67–9	2000
2,4-Dinitrophenol	51–28–5	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
bis(2-Ethylhexyl) phthalate	117–81–7	2000
Butyl benzyl phthalate	85–68–7	2000
Diethyl phthalate	84–66–2	2000
Dimethyl phthalate	131–11–3	2000
Di-n-butyl phthalate	84–74–2	2000
Di-n-octyl phthalate	117–84–0	2000

*Coelute

swatches were extracted and analyzed with the laundered swatches. The concentrations of the analytes of interest found on the control swatches after analysis was within 10% of the concentration originally applied. It was therefore assumed that the chemicals remained on the textiles and did not transfer to the foil during storage.

After application of the standards, blank swatches were pinned to the outside of large pieces (approximately 2′ × 3′) of outer shell fabric. Contaminated swatches were pinned to outer shell jackets (1–3 swatches per jacket). Two additional sets of turnout gear were used as ballast to increase the weight in each laundry load. All garments and fabric pieces were placed inside a Pellerin Milnor Extractor (Kenner, LA) Model 30022V8Z with MilTouch™ software control that includes an internal heater that maintains the programmed temperature throughout the cycle. Laundry cycles and g-forces were programmed into the software according to NFPA 1851 requirements. Duplicate programs were created to vary the temperature, and a soak cycle was added for this study. Table 2 provides the detailed methods used in the programmable extractor. Samples were laundered using these programs and the swatches were removed immediately at the end of the cycle and allowed to air dry on a drying rack. Three runs were laundered at each temperature with and without soak cycles for a total of 30 swatches and 3 blanks under each condition. Table 3 below shows the laundry matrix for the samples analyzed here.

A commercially available fire industry detergent containing D-limonene was used in all washings. Likewise, a commercially available fire industry soak solution containing D-limonene and 2-butoxyethanol was employed in the laundry runs that required a pre-soak. Both chemicals were used according to manufacturer directions found on the labels.

Table 2
Laundry Extractor Method

Laundry Cycle Parameters	Outer Shell (105°F, 125°F, 140°F & all cold water)	Outer Shell with Soak (105°F, 125°F & 140°F)
Wash—5 min (no chemical)	No	Yes
Soak—20 min with 500 ml of chemical (set temperature)	No	Yes
Extract—1 min	No	Yes
Rinse—10 min (hot and cold water—no set temperature)	No	Yes
Extract—1 min	Yes	Yes
Wash—15 min with 125 ml of chemical (set temperature)	Yes	Yes
Rinse—5 min (hot and cold water—no set temperature)	Yes	Yes
Extract—1 min	Yes	Yes
Rinse—5 min (cold water only)	Yes	Yes
Rinse—5 min (hot and cold water—no set temperature)	Yes	Yes
Final extract	Yes	Yes

Table 3
Laundry Matrix

	Swatches per cycle		Total analyzed per condition	
	Blanks	Swatches	Blanks	Swatches
All Cold	1	10	3	30
105°F	1	10	3	30
125°F	1	10	3	30
140°F	1	10	3	30
105°F + Soak	1	10	3	30
125°F + Soak	1	10	3	30
140°F + Soak	1	10	3	30

2.3. Sample Extraction

Several past studies have relied on extraction procedures described in EPA method 3500°C [37]. Although these extraction procedures were developed to remove semi-volatile organic compounds (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 was built on the combined aspects of these procedures to develop a method suitable for extracting contaminants from textiles.

Past studies have primarily used methylene chloride as the extraction solvent, however EPA 3500°C includes other solvents such as hexane, acetone, acetonitrile and cyclohexane as secondary extraction fluids or rinses. Recently, Banks et al. used a mixture of methylene chloride and toluene to extract PAHs from firefighter clothing [38]. Additionally, Mansoui and Zachariadis successfully extracted PAHs using solid-phase microextraction fibers (SPME) to extract PAHs from environmental matrices [39]. In order to streamline the extraction process and to extract chemical from multiple classes simultaneously (including PAHs, phthalates and phenols), a mixture of the following ratios was used here: 50% methylene chloride: 25% cyclohexane: 25% acetonitrile. This extraction method was developed and tested in prior work and is briefly described below [36].

Sample swatches were allowed to air dry after laundering and prior to chemical extraction. Each dry 7.6 cm × 15.2 cm swatch was cut into eight smaller squares and placed into a 300 mL Perfluoroalkoxy alkanes (PFA) vessel. Five ¾" diameter Teflon™ (PTFE) ball bearings and 50 mL of the solvent solution were added to the vessel. The vessel was capped tightly and placed on a Heidolf promax 2020 laboratory shaker at setting six (approximately 230 rpm) for 30 min. The PTFE 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 min 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-min time.) The samples were allowed to rest until the temperature of the liquid inside the vessel returned to room temperature (approximately 10–15 min).

A 45 mm glass fiber filter (GFF) was placed on the fritted surface of a glass filtration apparatus and connected to the laboratory vacuum line. Liquid 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 100 mL graduated oil tube for 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. These graduated conical tubes were ideal for concentrating samples given their taper lower shape and graduations. A mini-vap (MilliporeSigma) 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. The samples were gently condensed to ≤ 2.0 mL. The tubes were then removed from the rack and vortexed for 10–15 s to reincorporate solids dried on the sides of the tubes. Volume of the liquid samples were measured by drawing each sample into a graduated glass serological pipet. The sample was returned to the tube and an aliquot of the solvent mixture was added to the tube, which brought the final volume to 2.0 mL. The samples were vortexed again and then transferred to a 10 mL beaker. Each sample was then filtered into a pre-labeled 2.0 mL auto sampler vial using a 3 mL syringe with an attached polyvinylidene fluoride (PVDF) 0.45 µm syringe filter for analysis.

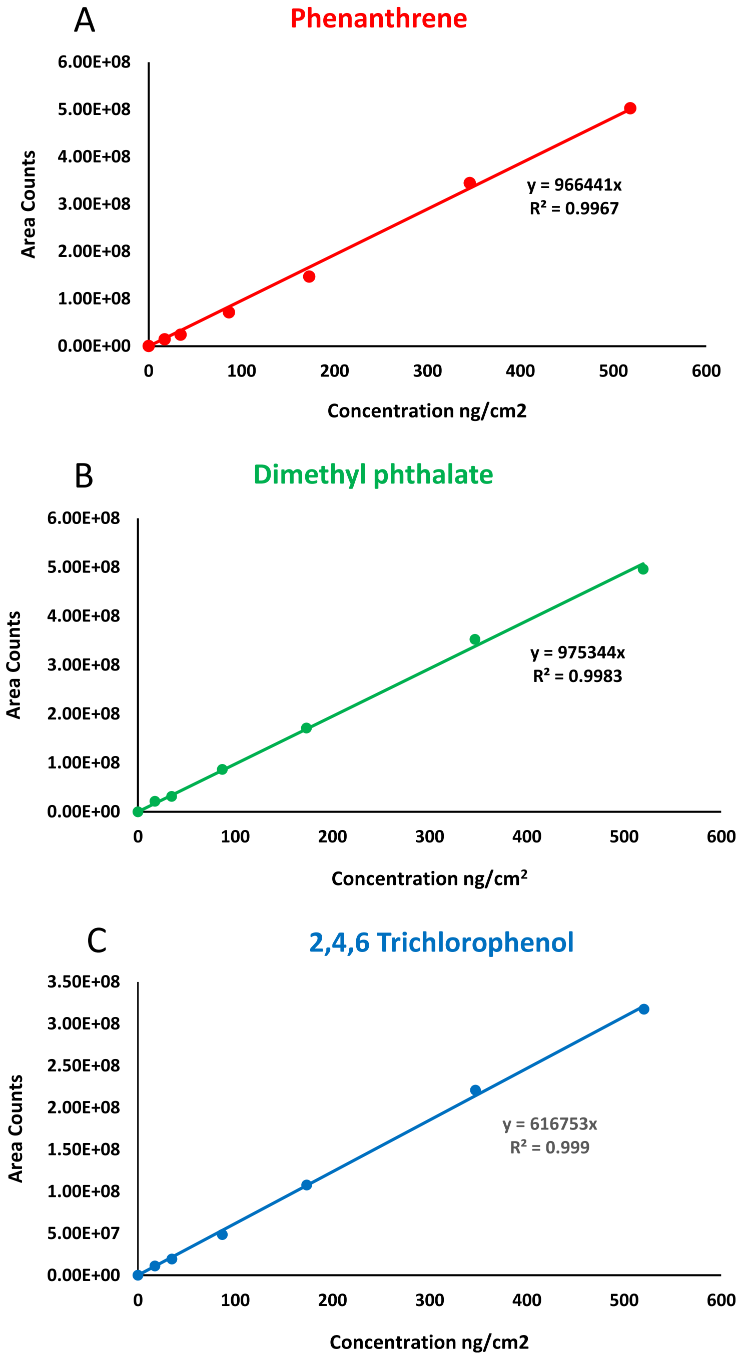
2.4. Sample Analysis

All samples were analyzed on a Thermo Scientific Trace 1310 gas-chromatograph connected to a Trace 8000 Evo triple quadrupole mass spectrometer. One microliter of sample was injected via a Thermo Scientific AI 1310 autosampler into a 200°C inlet containing a split/splitless straight with wool, Topaz® liner (Restek). A Restek Rxi®-5Sil MS w/Integra Guard, 30 m, 0.25 mm ID, 0.50 µm column was used to achieve separation. The oven temperature was held at 60°C for 2 min after injection then the temperature was ramped at a rate of 7°C per minute until 310°C with a 10-min hold. The temperature of the transfer line and ion source were 300°C.

Data was integrated using Xcalibur software when possible. In the event of interference or over-lapping peaks, the peaks were manually integrated.

3. Results

A five-point calibration curve was analyzed for each analyte of interest here. As stated earlier, the swatches for the calibration curve were coated and extracted using the same methods as the swatches for analysis. This eliminated the need for matrix spikes and assumed any losses would be uniform between the calibration swatches and sample swatches and detailed in previous work [36]. Fig. 1 shows representative calibration curves plotted as concentration (ng/cm^2) vs. peak area


A
Phenanthrene
Area Counts
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
0
100
200
300
400
500
600
Concentration ng/cm2
y = 966441x
R² = 0.9967
B
Dimethyl phthalate
Area Counts
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
0
100
200
300
400
500
600
Concentration ng/cm²
y = 975344x
R² = 0.9983
C
2,4,6 Trichlorophenol
Area Counts
3.50E+08
3.00E+08
2.50E+08
2.00E+08
1.50E+08
1.00E+08
5.00E+07
0.00E+00
0
100
200
300
400
500
600
Concentration ng/cm2
y = 616753x
R² = 0.999

◀**Figure. 1. Calibration curves for select chemicals from the classes investigated here: (A) Phenanthrene; (B) Dimethyl phthalate; (C) 2,4,6 Trichlorophenol.**

counts for the chemicals in this study. Limits of detection were calculated for all compounds discussed in this work and were in a range of 10–20 ng/cm^2.

All contaminated swatches, blanks and calibration curve samples were analyzed and 8 were chosen for quantification in this study: 2,4,6 trichlorophenol, 2,4,5 trichlorophenol, dimethyl phthalate, phenanthrene, di-n-octyl phthalate, pyrene, chrysene and benzo(a)pyrene. Additional chemicals, i.e. phenol, 2-chlorophenol, 2-methylphenol 2,4-dimethylphenol, 2,4-dichlorophenol, naphthalene, acenaphthylene, and diethyl phthalate were quantified but all had a removal efficiency at 105°F and 125°F of 95% or greater and were not included in the data tables. The choice of quantification analytes was based on chromatography and interferences from coatings applied to the outer shell textiles. One blank sample was laundered and analyzed with each set of swatches. None of the compounds from the multi-chemical standard were found on any of the blanks indicating that there was no cross-contamination in the laundering process.

Table 4 below shows the average results of analytes remaining on the swatches under each laundry condition as a heat map. Table 5 (also heat map) contains the percent removal of chemicals based on control (unlaundered) swatches that were analyzed in conjunction with the laundered swatches. Actual concentration and percentage data used to generate these heat maps can be found in the supplemental information. As anticipated, the data shows an overall trend where the compounds with the highest molecular weights also have the lowest percent removal. The solubility of these SVOCs tends to decrease as the molecular weights increase. Table 6 contains the structures, molecular weights and octanol–water coefficients (LogP) for the chemicals selected. [40, 41] In fact, Johnson, et al. found that the aqueous solubility of PAHs decreases almost logarithmically with increasing molecular weight [42]. The results from this study suggest that the percent removal of the individual compounds increases as the water temperature increases. With the addition of the soak step, the solubility of the larger compounds (primarily PAHs) increases, therefore, the percent removal increases by $>$ 15% for all chemicals at the NFPA specified maximum temperature of 105°F.

4. Discussion

The NFPA 1851 standard recommends that the maximum temperature to which turnout gear should be exposed during the laundering and drying processes is 105°F. This temperature was originally established to prevent burns to the hands of service personnel who hand launder the gear in a utility sink and on recommendations from textile and reflective trim manufacturers and suppliers [43]. There are also restrictions on pH of the laundry detergent and the addition of solvents to prevent degradation of certain gear materials and trim components. [44]

Table 4
Concentrations of Chemicals Remaining After Laundering (ng/ cm^2 ± SE)

Water Temperature	Dimethyl phthalate	2,4,6-Trichlorophenol	2,4,5-Trichlorophenol	Phenanthrene	Di-n-octyl phthalate	Pyrene	Chrysene	Benz(a) pyrene
All Cold	0	39	55	170	205	278	283	301
105°F	0	32	44	186	216	239	282	306
125°F	0	11	18	134	192	215	255	312
140°F	0	0	0	63	184	145	173	234
105°F Soak	0	0	0	122	173	180	223	227
125°F Soak	0	0	0	80	155	156	190	229
140°F Soak	0	0	0	54	138	128	149	186
MDL µg/cm²	13	10	16	16	26	18	17	51

ND non-detect or below the MDL for that chemical
n = 30

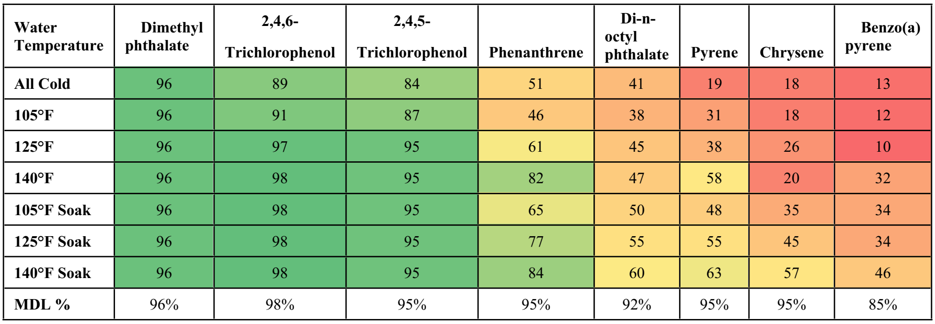
In this work we compared cleaning efficiencies at the recommended temperature of 105°F and with elevated temperatures of 125°F and 140°F and an "all cold" wash that was dependent on outside conditions with temperatures averaging 70°–75°F.

Initial experiments were conducted using a programmable extractor with no internal heater or steam option. The in-line water heater was located in an interior corridor at the NIOSH Morgantown facility and was set to provide water to the extractor at a temperature of 180°F. Temperature programs were set, measured and monitored using a submersible data logger (Onset, Bourne, MA) in the extractor. This was performed in the early summer where outdoor temperatures in West Virginia range from 50°F to 80°F. Data was consistent between runs throughout the summer.

This temperature study began in January when temperatures frequently vary from 0°F to 35° F. When laundry cycles were run to verify the temperatures prior to the start of the study, the data from the logger was reviewed, and it became apparent that the set temperatures could not be maintained. The outdoor temperature was 7°F on the day the readings were taken. Figure 2 below shows a series of consecutive washes using the 140°F cycle. We determined that an extractor with an internal heater or steam injector is required to maintain constant temperatures over several runs. For this reason, a new Pellerin Milnor extractor described in the sample preparation section was purchased and used for the work described here.

An additional wash cycle using only cold water (average temperature 70°–75°F) was added to this study because of the outdoor temperature fluctuations. This was intended to simulate launderings in areas where cold temperatures are prevalent. This could also mimic conditions in a firehouse when hot water is in a higher demand following a fire event. Additional showers, laundry runs and other activi-

Table 5
Percent Removal Efficiencies of Select Organic Compounds



Water Temperature	Dimethyl phthalate	2,4,6-Trichlorophenol	2,4,5-Trichlorophenol	Phenanthrene	Di-n-octyl phthalate	Pyrene	Chrysene	Benzo(a) pyrene
All Cold	96	89	84	51	41	19	18	13
105°F	96	91	87	46	38	31	18	12
125°F	96	97	95	61	45	38	26	10
140°F	96	98	95	82	47	58	20	32
105°F Soak	96	98	95	65	50	48	35	34
125°F Soak	96	98	95	77	55	55	45	34
140°F Soak	96	98	95	84	60	63	57	46
MDL %	96%	98%	95%	95%	92%	95%	95%	85%

n = 30

ties may prevent the water heater from maintaining a constant supply of hot water.

Chemicals are released from combusted materials due to the high temperatures during a fire. These chemicals may travel on air currents, adhere to soot or deposit on surfaces. When these chemicals adsorb to outer shell garments through surface deposition, through van der Waals forces or by bonding with the chemicals applied as protective coatings on the surface of the garment. These bonds may range from ionic to covalent and are a dissociative chemisorption process. These chemicals may remain on the surface until they are desorbed by heat or ionic interactions. Additional investigations into these surface interactions should be conducted. The data from the study here shows that these bonds are more likely to break at elevated temperatures.

Once the chemicals are bound to the surface, external forces such as temperature increases or chemical reactions are required to break the newly formed bonds. In some instances, a higher water temperature will provide enough energy to break chemical bonds. Laundry detergents are amphipathic molecules that contain polar hydrophilic heads and hydrophobic tails. These molecules orient to form micelles which trap hydrophobic molecules and enable them to be removed from surfaces of the textiles and partition into the water [45].

To overcome the surface bonding, wash temperatures were increased in this study and a solvent based soak solution was employed. The heat maps in Tables 4 and 5 show that these new methods increased the cleaning efficiencies of most of the chemicals studied here with the exception of dimethyl phthalate which was removed at a $> 99\%$ efficiency in all laundry conditions. These chemicals will be discussed in detail below.

4.1. Dimethyl Phthalate

Dimethyl phthalate is not classifed by IARC for carcinogenicity properties. It is found in plastics and rubber coatings and is used as a pesticide and insecticide

Table 6
Selected Chemicals, Physical Properties and Structures

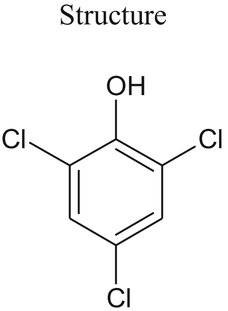
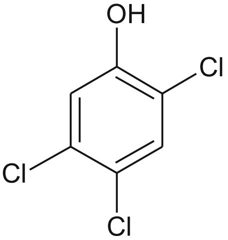
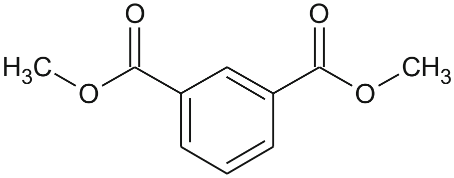
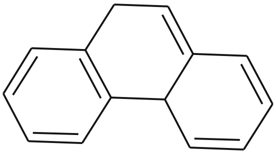
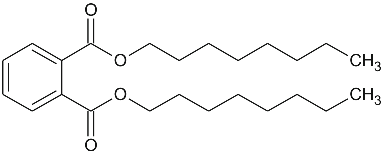
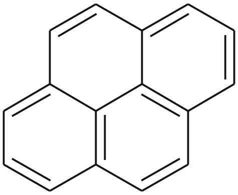
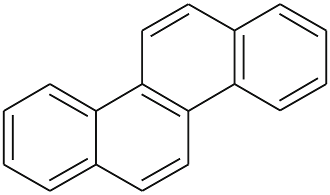
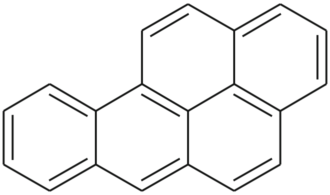
Compound	Octanol–Water Partition Coefficient (LogP)*	Molecular Weight (amu)	Structure
2,4,6-Trichlorophenol	3.7	197.45	
2,4,5-Trichlorophenol	3.7	197.45	
Dimethyl phthalate	1.6	194.2	
Phenanthrene	4.5	180.2	
Di-n-octyl phthalate	9.1	390.6	

Table 6 continued

Compound	Octanol–Water Partition Coefficient (LogP)*	Molecular Weight (amu)	Structure
Pyrene	4.9	202.2	
Chrysene	5.7	228.3	
Benzo(a)pyrene	6	252.3	

*Computed by XLogP3 3.0 (PubChem release 2021.05.07)

[40]. As stated previously, dimethyl phthalate was not detected in any laundry experiment, therefore temperatures of 105°F and a commercial detergent are sufficient for its removal.

4.2. Chlorinated Phenols

2,4,6-Trichlorphenol is classified as a probable human carcinogen (*Group* 2B) by IARC. 2,4,6-trichlorophenol was used primarily as a pesticide, herbicide and wood preservative and is use had decreased in recent years in the United States [40]. 2,4,5-Trichlorophenol is not classified by IARC for carcinogenicityand is primarily used as a pesticide [40]. Both 2,4,5- and 2,4,6-trichlorophenol had cleaning efficiencies of 95% or greater by increasing the temperature to 125°F. When laundered at 105°F with the addition of a pre-soak, neither chemical was detected on the swatches.

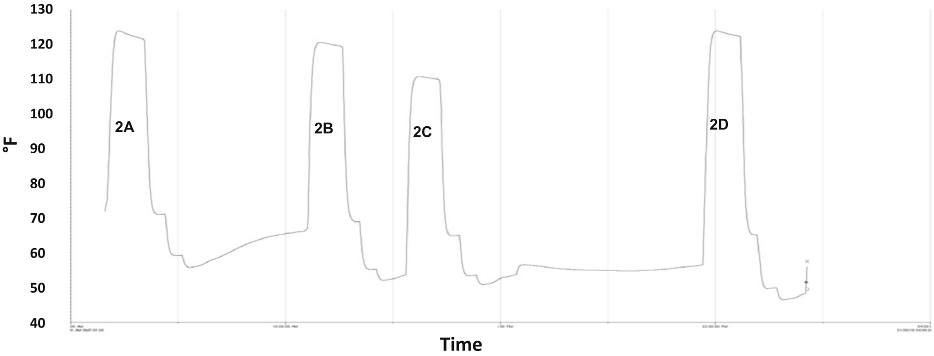


Figure. 2. Temperature profiles of consecutive washes programmed at 140°F with an outdoor temperature of 7°F. (A) Water only, maximum temperature reached 123°F; (B) Water plus dry gear, maximum temperature reached 120°F; (C) Water plus wet gear, maximum temperature reached 110°F; (D) Water plus gear warmed in dryer, maximum temperature reached 124°F.

4.3. Phenanthrene

Phenanthrene is classed by IARC as a *Group 3* chemical, not classifiable as a human carcinogen due to insufficient human and animal studies for a conclusive human carcinogen classification. Phenanthrene is a naturally emitted source from biomass combustion and coal tar [40]. Phenanthrene had the highest percent removal, from 46% at 105°F to 84% at 140 °F with a pre-soak, of all of the PAHs studied here. As with the other PAHs discussed below, the percent removal increased with temperature and a pre-soak cycle.

4.4. Di-n-octyl phthalate

Di-n-octyl phthalate (DNOP) has not been reviewed by IARC to determine carcinogenicity. It is widely used as a plasticizer in products such as medical tubing and bags, carpet backing, wire coatings, floor tile and adhesives. DNOP showed only a 38% to 47% cleaning efficiency on cleaning cycles up to 140°F but improved from 50 to 60% in cycles when a soaking step was added.

4.5. Pyrene & Chrysene

Pyrene is classed by IARC as *Group 3* chemical. Pyrene is found in the environment as an product of incomplete combutsion [40]. Chrysene is classed as a Group 2B substance, possible human carcinogen. Chrysene is ubiquitous in the environment and is also a product of combustion [40]. Both of these compounds showed low (18%) cleaning efficiencies in cold water. However, cleaning efficiencies increased with temperature and further increased with the addition of the soak cycle from 19% at 75°F to 63% at 140°F with a pre-soak cycle.

4.6. Benzo(a)pyrene

Benzo(a)pyrene (BaP) is a PAH comprised of 5 benzene rings. It is insoluble in water at room temperature but soluble in a number of organic solvents including methylene chloride. BaP is classified as a *Group 1* carcinogen by IARC, meaning it is recognized as being carcinogenic to humans [46]. BaP is a by-product of combustion of wood and wood products, exhaust emissions and cigarette smoke [40]. It has the highest boiling point of the chemicals studied here and had the lowest cleaning efficiency of all compounds. In normal laundry processes using all cold water (70–75°F) and temperatures of 105°F and 125°F, the percent removal only varied by 2%. However, when the temperature was increased to 140° or in any cycle where a pre-soak was carried out, the cleaning efficiency increased by 20% to 35%

5. Conclusions

This study was designed to test the NFPA 1851 guidance for cleaning of firefighter textiles to determine if the current guidance is adequate or if changes to the standard should be made. In the standard, the choice of laundry detergent is at the discretion of the laundry facility, therefore a common commercial fire soap formulation was used. Swatches were laundered using the current guidance and at elevated temperatures to determine if the higher temperatures increased solubility. A pre-soak step was added to the method using a commercial degreaser to determine if the chemicals in that formulation increased solubility. The results from this study show that increased temperatures result in higher cleaning efficiencies for several selected SVOCs. The addition of a pre-soak with agitation at the same temperature further increases the cleaning efficiencies of the SVOCs studied here. The selected phthalates and chlorinated phenols had cleaning efficiencies of 95% or above with a 20°F increase in laundry temperature or at a temperature of 105°F with a pre-soak cycle. Additional work will need to be conducted to study higher molecular weight persistent PAHs. Also, other soak solutions should be investigated to determine the best formulation for removal of PAHs. To determine if chemisorption is the process by which the contaminants are adsorbed to the fabrics, soiled gear containing soot should be evaluated to determine the interactions between chemicals deposited on the surface, soot and the DWR chemicals applied during manufacturing. In addition, these experiments should be repeated using swatches of fabric laundered multiple times to investigate the chemisorption theory.

Fire stations that launder their own gear should monitor laundry temperatures to ensure that they are able to maintain at least 105°F for the entire cycle. If they are located in an area where temperatures are often below freezing or if they are unable to maintain temperatures of at least 105°F, a commercial laundry service may be an option for more effective removal of fireground contaminants.

The findings and conclusions in this report are those of the author(s) and do not necessarily represent the official position of the National Institute for Occupa-

tional Safety and Health, Centers for Disease Control and Prevention. Mention of any company or product does not constitute endorsement by NIOSH, CDC.

Declarations

Conflict of interest Authors certify that they have no financial or proprietary interests in any material discussed in this article.

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SUPPLEMENTARY INFORMATION

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