Firefighter Turnout Gear SVOC Cleaning Efficiency of CO2-Based Cleaning Process Compared to Traditional Water-Based Cleaning Methods

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Firefighting is dangerous work. In the process of doing their jobs, firefighters are frequently exposed to many hazardous chemicals including metals, volatile organic compounds (VOC), Polycyclic aromatic hydrocarbons (PAH), and other semi volatile organic compounds (SVOC). Many studies have shown that substantial quantities of organic compounds can be found on the turnout gear used by firefighters after responding to a fire emergency. The exposure routes of concern for firefighters are inhalation, dermal and oral routes. These exposures have been proven to lead to a variety of cancers and other illnesses.

Firefighter turnout gear is necessarily complex, as it is designed to protect the firefighter from heat, steam, puncture, and other hazards, yet cool enough to be worn during the hottest of fire events. Turnout gear consists of four (4) distinct layers; an outer layer, moisture barrier, thermal layer, and lining. Typically, the turnout gear is expensive, costing $2500 or more per set.

Previous studies have shown that after a fire incident there can be substantial quantities of toxic organic compounds deposited on firefighter turnout gear. After interior firefighting incidents and periodically through the year, the firefighter turnout gear is cleaned; typically, with an in-house water wash extractor system or outsourced to professional cleaner services that also use water-based cleaning methods.

To evaluate the effectiveness of water-based cleaning methods on firefighter turnout gear, a detailed study was conducted in Finland by the Finnish Institute of Occupational Health [1]. This study evaluated the source of contamination from numerous firefighter events, the type and location of organic toxins on the gear, and the effectiveness of traditional water-based cleaning systems in removing these hazardous compounds. The study concluded:

- PAHs were found throughout the turnout gear in concentrations that exceeded safety standards;
- Substantial VOC and SVOC concentrations were found in the moisture barrier layers of the gear;
- The highest concentration of ions was found on the inner thermal barrier layers of the gear from HCL products of burning PVC plastic;
- Water washing did a poor job of removing PAHs and was responsible for transferring more contamination on the gear to less contaminated areas.
    - Washing two (2) garments yielded a washing efficiency of 40%;

- Washing three (3) garments yielded a washing efficiency of 15%.

In another study, the effectiveness of water-wash cleaning to remove PAHs from firefighter hoods was evaluated. They found that the removal efficiency of this process for all PAHs was 75.5% [2].

To address the known accumulations of products of incomplete combustion firefighters are exposed to, recent NFPA guidance recommends frequent advanced cleaning of turnout gear – at least twice per year and/or soon after significant fire events. The typical cleaning method involves variations of industrial washers, using hot water, industrial detergents, and customized dryers. In Europe, cleaning standards have been developed for individual countries such as Germany [3]and those in the EU [4]. In the USA, the standards for cleaning the gear is outlined in NFPA 1851 [5]. The NFPA standard details a specific method to test and validate the cleaning efficacy of cleaning systems to remove a list of hazardous compounds from firefighter turnout gear.

These and other studies all conclude that while the water wash system removes some of these hazardous compounds, they leave behind substantial quantities of these toxic materials. To address this deficiency on firefighter turnout gear, alternative technologies have been introduced to improve the cleaning.

Carbon Dioxide (CO_2) cleaning and extraction systems produced by Cool Clean Technologies have been used for decades to clean difficult and complex materials in aerospace, medical, industrial, and agricultural applications. Recently CO_2 cleaning has been applied specifically to cleaning firefighter turnout gear in Europe [6]. In this study, the researchers obtained a contaminated piece of turnout gear – a coat – cut it in half, cleaned one half in a standard water-wash cleaning system and the other half with a CO_2-based cleaning system – similar to the Cool Clean Technologies manufactured system. Samples of each layer of the turnout were evaluated before and after cleaning. The results from this study showed:

- The gear contains toxic products that are present in a significantly higher concentration in the clothing than legally permitted in Europe.
- 87% of these toxic products are in the outer layer and the moisture barrier.
- Industrial cleaning with water and detergents according to the ISO 6330 standard gives a cleaning efficiency (=chemical decontamination) of 27.4%.
- Industrial cleaning according to the CO_2 cleaning technology gives a cleaning efficiency of 98.9%.

While the results of the CENTEXBEL study are very important, this study did not follow the standard testing and evaluation protocols outlined in the NFPA standard.

Contaminants Investigated

The analytical part of this test is governed entirely by the NFPA method [5]. The method identifies a list of ten (10) target SVOC contaminants of interest:

- Ten (10) SVOCs – Acenaphthene (CAS No. 83-32-9), Anthracene (CAS No. 120-12-7), Diethyl phthalate (CAS No. 84-66-2), Di-n-octyl phthalate (CAS No. 117-84-0), Fluorene (CAS No. 86-73-7), Phenanthrene (CAS No. 85-01-8), Pyrene (CAS No. 129-00-0), 2-Nitrophenol (CAS No. 88-75-5), Phenol (CAS No. 108-95-2), 2,4,6-Trichlorophenol (CAS No. 88-06-2).

The NFPA standard details the analytical test method to be used to collect and analyze each chemical, how each test swatch is doped (quantity and concentration of each chemical), how the test swatches are to be stored, and how they are analyzed and reported.

Study Objective

The objective of this study is to measure the cleaning efficacy of two (2) CO2-based cleaning systems for removal of NFPA target SVOCs using test methodologies that follow the NFPA guidelines. The results of this study can be used by those responsible for firefighter safety to determine the best cleaning options for the firefighter turnout gear.

Experimental Test Methods

Details of the test methods used to quantify the results from this study are presented below.

CO2 Cleaning Systems Used in Study

Numerous CO2-based cleaning systems have been developed to remove a wide range of contaminants from numerous articles. The CO2+ system which has been used for over 20 years to clean a wide range of textiles and other substrates was used in this study. This system uses an environmentally friendly cleaning solvent used in a wide range of household products to clean the materials followed by a Liquid CO2 (LCO2) wash system. The resulting process provides excellent cleaning performance without damage to the articles cleaned. The graphic in Figure 1 shows the process steps of the CO2+ Cleaning System.

At the conclusion of the CO2+ process typically 40 – 70 minutes in duration, the contents are removed – with no additional drying required. The CO2+ Cleaning system is shown in Figure 2.

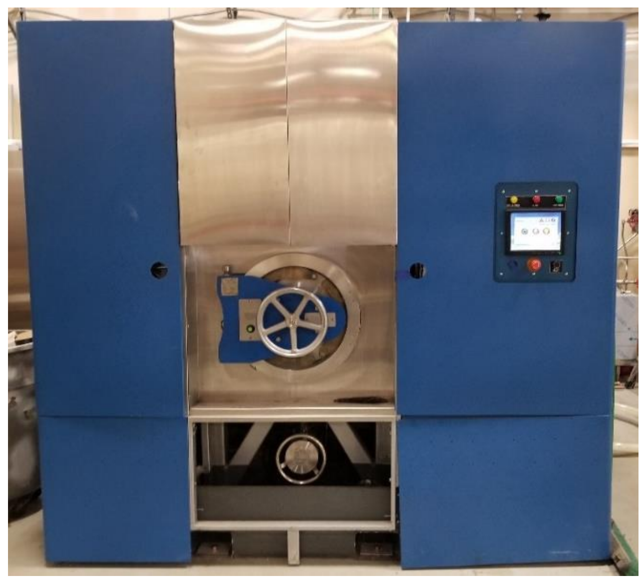

Figure 2 – CO2+ Cleaning System used in this study.

Figure 1 – CO2+ Process Steps

A summary of the key run parameters for each cleaning system is presented below in Table 1.

Table 1 – Run Parameters for CO2+ and Water Wash Test reported.

Run Parameter	CO2+	Water Wash
Number of cleaning baths	1	1
Duration of clean bath	6	8
Number of rinse baths	5	4
Duration rinse baths	15	2
Run Duration, min	55	22
Average CO2 pressure during cleaning / rinsing, psig	542	0
Average temperature during cleaning, °F	49	105
CO2 Used for Cleaning, lb	225	NA
CO2 Vented per cycle, lb	20	NA
Additive type	None	Reliant
Additive quantity	Na	1 fl oz
Drying Time	45 min	Overnight

Water Wash System Used

A UniMac 65 lb Capacity High Performance Industrial Washer Extractor System shown in Figure 3 was used as the water-wash system in this study. A summary of the system operating conditions is also presented in Table 1.

Figure 3 – UniMac 65 Industrial Water Wash Extractor System

Determination of a standard NFPA wash load.

The NFPA method also identifies the specifics on how the wash load to be examined is to be developed. This includes the following:

- Definition of type of surrogate turnout gear to be used.
  - Type of material used
  - Size and shape of gear, number, and location of pockets
- Where and how test swatches are to be inserted into pocket
- Definition of panels for ballast for tests
  - Type of ballast material to be used
  - Exact shape, size of panel
- Definition of order loading surrogate gear into the wash vessel.

As part of the test documentation, photos before and after the cleaning tests are taken.

Analytical Methods

The analytical test results for this study are presented below for each cleaning system evaluated. The analytical testing and analysis are specified and detailed in the NFPA Standard [7]. The standard details not only the chemicals to examine, but also the specific analytical testing methods to be used for NFPA-1851 compliant test methodologies. The chemical / analytical results were generated by Legend Technical Services of St. Paul, MN. An important part of interpreting these results is an understanding of the reference detection level (RDL) of a chemical, the quantity applied, and the quantity recovered from a recovery test.

The RDL is a mass concentration of an individual chemical below which the method cannot accurately quantify – hence is a 'non-detect'. For the SVOCs analyzed in these tests, the RDLs are 3.1 or 1.5 µg/gm, depending on the chemical, as shown in Table 2 below. Hence a reported concentration of '<3.1 µg/gm' is interpreted as 'non-detect'. This does not mean that the result is absolutely zero (0), only that the test result was below the detectable level. Nevertheless, when displaying or averaging these analytical results below the RDLs, they are assumed to be zero (0).

Table 2 – Mass Recovery Values Used for Data Analysis

Analyte	Units	RDL, ug/gm	Mass Applied, ug/gm	Mass Recovered* ug/gm	Recovery Efficiency, %
Phenol	ug/g	3.1	18	17	94%
2-Nitrophenol	ug/g	3.1	18	15	83%
2,4,6-Trichlorophenol	ug/g	3.1	18	18	100%
Acenaphthene	ug/g	1.5	18	16	89%
Fluorene	ug/g	1.5	18	16	89%
Diethyl phthalate	ug/g	1.5	18	17	94%
Phenanthrene	ug/g	1.5	18	16	89%
Anthracene	ug/g	1.5	18	16	89%
Pyrene	ug/g	1.5	18	16	89%
Di-n-octyl phthalate	ug/g	1.5	18	16	89%
Average SVOC			18	16.3	91%
* - Used for Recovery Efficacy Test Result Determination					

The quantity of contaminant applied to the test swatch is specified in the method; 18 µg/gm for SVOCs, as specified in the NFPA 1851 method. The recovery efficiency of the analytical method for an individual contaminant represents the efficiency of capturing the applied quantity of the contaminant; a 90% efficiency means that the method was able to quantify or 'see' 90% of the applied material. The effective quantity of an individual contaminant that is 'available' for detection is the quantity recovered in the method, not the quantity applied. Hence, when determining the collection efficacy of a contaminant, the mass found in the recovery efficiency testing will be used, not the mass applied, as shown in Table 2.

Method Overview and Summary

Based on the detail provided above, the results following will provide a systematic method to compare the SVOC cleaning effectiveness of various cleaning technologies and their ultimate value to the firefighter and those charged with their health and safety.

Test Results

The test results for this study are presented below for each cleaning system evaluated. The results from the NFPA Water Wash and CO2+ tests are summarized in Table 3 below. Examining the Water Wash SVOC results, the average cleaning efficacy was 66%, but ranged from a low of only 9% Di-n-octyl phthalate to 100% for 2,4,6-Trichlorophenol, 2-Nitrophenol and Phenol, the most volatile compounds of the SVOCs tested. The CO2+ SVOC tests show samples cleaned generated 'Non-Detect' for all SVOCs tests. Hence the cleaning efficacy was 100% for all SVOCs tested.

Table 3 – NFPA SVOC Cleaning Efficiency: Water Wash vs CO2+

SVOC	Water Wash	CO2+
Phenol	100%	100%
2-Nitrophenol	100%	100%
2,4,6-Trichlorophenol	100%	100%
Acenaphthene (PAH)	78%	100%
Fluorene (PAH)	63%	100%
Diethyl phthalate	90%	100%
Phenanthrene (PAH)	40%	100%
Anthracene (PAH)	43%	100%
Pyrene (PAH)	27%	100%
Di-n-octyl phthalate	9%	100%
Average SVOC	66%	100%

Discussion of Results

Cleaning System Comparison of NFPA Cleaning Efficiency

It is useful to examine the SVOC cleaning Efficiency for the different cleaning options. A graph of Residual SVOC Contaminants is presented in Figure 4. In effect, this graph is the complement of SVOC data shown in the earlier graphs. Another way of looking at these results is to examine the percentage improvement in cleaning Efficiency of the CO2+ system compared to the water wash systems.

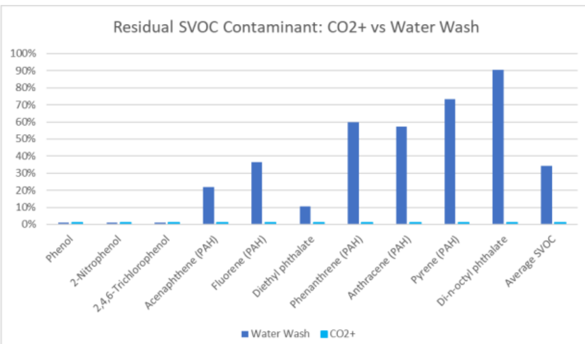

Figure 4 – Comparison of SVOC Residuals for the three cleaning systems examined.

To identify the importance in cleanliness Efficiency of various contaminants, it is useful to examine the health impact of specific contaminants. Data was compiled by EPA to obtain Human Health Benchmark which combines oral reference doses (RfDs), inhalation reference concentrations (RfCs), oral cancer slope factors (CSFs), and inhalation CSFs to obtain a 'health benchmark' by chemical. In some cases, NOAEL (No Observed Adverse Effect Level) values were used, which denotes the level of exposure of an organism, found by experiment or observation, at which there is no biologically or statistically significant increase in the frequency or severity of any adverse effects of the tested protocol. The data is presented in Table 4 below.

The data was collected and compared to the SVOC test results for water washing. The data shows the relative importance of specific contaminant removal and the impact of not removing the compounds. For example, the most hazardous SVOCs contaminant examined is Phenanthrene and Acenaphthene with TEF values of 0.001 mg/kg/day. Note that for Acenaphthene, with only 3.5 mg/kg recover on the test swatch, a relative hazard impact is estimated at 3500. By contrast, Di-n-octyl phthalate residues are the largest found on the swatch but generate a hazard index of only 725. Using this standard, the most hazardous compound found among the SVOCs tests is Pyrene, with an estimated hazard impact of almost 12,000. While the hazard impact metric proposed is not an exact measure of human hazard, it is useful to identify the importance of removing the most hazardous chemicals from the turnout gear.

Table 4 – Hazard Impact Estimate of SVOC Residues Remaining on Test Swatches after NFPA Water Wash Tests

Contaminant	Cancer Ranking	Cleaned Swatch Result, mg/kg	EPA Human Health Benchmark RfD [8], RfC, oral CSF, inhalation CSF (mg/kg/d)	Hazard Impact: Contaminant Mass Collected / RfD, TEF
Phenol		0	0.6 - RfD	0
2-Nitrophenol		0	0.25*	0
2,4,6-Trichlorophenol	RAHC	0	0.01 CSF inh	0
Acenaphthene (PAH)	RAHC	3.5	0.001 - TEF	3500
Fluorene (PAH)	RAHC	5.85	0.04 - RfD	5850
Diethyl phthalate		1.775	0.8 - RfD	2
Phenanthrene (PAH)	RAHC	9.55	0.001 - TEF	9550
Anthracene (PAH)	RAHC	9.15	0.01 - TEF	915
Pyrene (PAH)	RAHC	11.75	0.03 - TEF	11750
Di-n-octyl phthalate		14.5	0.02 - RfD	725
RAHC – Reasonably anticipated to be human carcinogen				
RfD - oral reference doses (RfDs),				
RfC - inhalation reference concentrations (RfCs),				
CSF - cancer slope factors, inhalation and oral				
TEF – toxicity equivalency factor				
* - Obtained by scaling NOAEL of 0.89 mg/m^3 assuming an air volume per day of 20 m^3/day and a nominal body mass of 70 kg.				

An examination of the SVOC results presented in Table 3 shows that the phenol groups are efficiently removed by both the Water Wash and CO2+ process. However, the polycyclic aromatic hydrocarbons (PAHs) show substantial residues remaining on the test swatches after Water Wash - over 50% on average of the applied PAH remaining on the test swatch, as shown in Figure 5. These results are significant as the PAH compounds are the most hazardous SVOCs on the NFPA list, as shown in Table 4.

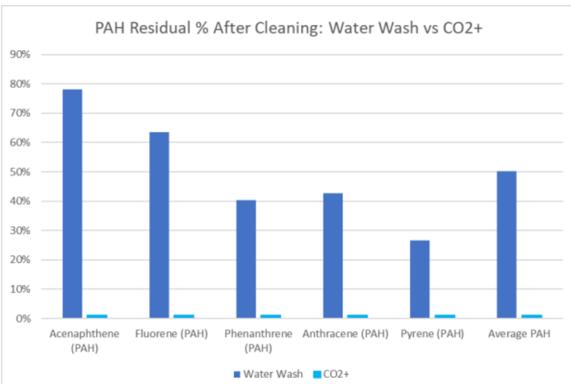

Figure 5 – PAH residues found on NFPA test swatches after Water Wash process – Note CO2+ process registered NON-DETECT values for all PAHs tested.

The two phthalate compounds are also of interest in this examination. Figure 6 shows the residuals of the two phthalates tested – showing residuals ranging from 10 – 90%. The implication of the results in Table 3 is that the CO2+ cleaning processes removed specified NFPA specified SVOCs, and in particular PAHs, to a non-detect level in all cases, demonstrating the superiority of the CO2+ process in removing hazardous SVOCs.

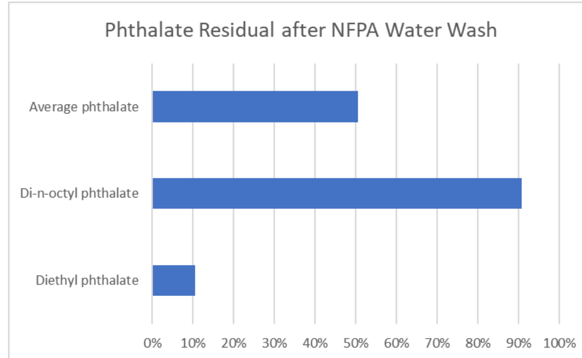

Figure 6 –Phthalate residues found on NFPA test swatches after Water Wash process – Note CO2+ process registered NON-DETECT values for all phthalates tested.

Summary

This report summarizes a test program which evaluates two different cleaning systems and their Efficiency on removing hazardous compounds from firefighter turnout gear. The methodology used to generate these results follows NFPA standards. Using these standards, results presented herein show that the industry standard water wash system testing left behind about 50% of the applied PAHs on the test swatches. These results support those of others which demonstrate that CO2 cleaning systems tested show superior SVOC cleaning efficiency relative to the industry standard water wash system.

For further information:

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References

1. Contamination and decontamination of firefighting garments –Laboratory tests, Finnish Institute of Occupation Health, Laitinen J, Tuomi T, Vainiotalo S, Laaja T, Rantio T,Parshintsev E, Kiviranta H, Koponen J, Pyrstöjärvi P,Kemmeren M, Heus R.
2. Firefighter hood contamination: Efficiency of laundering to remove PAHs and FRs; Alexander C. Mayera , Kenneth W. Fent, Stephen Bertke, Gavin P. Horn, Denise L. Smith,Steve Kerber, and Mark J. La Guardia; JOURNAL OF OCCUPATIONAL AND ENVIRONMENTAL HYGIENE; 2019, VOL. 16, NO. 2, 129–140.
3. German GS-Mark (German Committee for product Safety) has also established a limit value for the above-mentioned PAHs being 0.5 mg/kg (12.5 ng/cm2). They have also given a limit value of 10 mg/kg (250 ng/cm2) for the sum of the 18 PAHs being in category 2. This category is provided for material with foreseeable contact to skin longer than 30 seconds (long- term skin contact).
4. EU commission has given regulation No 1272/2013 for the content of PAHs in different materials. PAHs content 1 mg/kg (25 ng/cm2) of benzo[a]pyrene, benzo[e]pyrene, benzo[a]anthracene, crysene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene and dibentzo[a,h]antracene in the articles should not be exceeded.
5. NFPA 1851 – Standard on Selection, Care, and Maintenance of Protective Ensembles for Structural Fire Fighting and Proximity Fire Fighting, 2020.
6. - CENTEXBEL NFPA 1851 Chemical Decontamination Efficacy Test, 2019.
7. NFPA 1851 – Standard on Selection, Care, and Maintenance of Protective Ensembles for Structural Fire Fighting and Proximity Fire Fighting, 2020; Section 12.4.
8. https://archive.epa.gov/epawaste/hazard/web/pdf/2-chap15.pdf