Removal of PFAS Compounds from Firefighter Gear using CO2+ Cleaning Technology: A Summary of Preliminary Test Results

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INTRODUCTION: Carbon Dioxide (CO2) based cleaning technologies have been used for decades to solve innovative and complex cleaning and extraction challenges. Liquid CO2 (LCO2) cleaning systems were developed in the early 1990's as an alternative to traditional dry-cleaning systems. These early systems have evolved to be capable of effective cleaning and decontaminating firefighter gear. Cool Clean Technologies LLC (CCT) LCO2 based system "CO2-Plus" CO2+ has demonstrated superior SVOC/PAH removal of 99+% and shown effective removal of metals and biologicals based on numerous tests and designation by National Fire Protection Association (NFPA) as certified to clean and inspect firefighter gear. Expanding on these achievements, CCT performed initial tests to evaluate the effectiveness of removing selective per-and polyfluoroalkyl substances (PFAS) compounds from test swatches. These tests were performed mirroring the NFPA 1851 protocols.

BACKGROUND AND OBJECTIVES: The CO2+ cleaning process used for these tests depicted in Figure 1 below. This system uses an environmentally friendly cleaning trade secrete solvent (CoolCare™) to clean the materials followed by a Liquid CO2 (LCO2) rinse cycle. The resulting process provides excellent cleaning performance without damage to the articles cleaned. At the conclusion of the CO2+ process, typically 40-70 minutes in duration, the contents are removed with no additional drying required. Furthermore, the residues removed from the gear are concentrated in the still bottoms and filter media, which are subsequently disposed as hazardous waste and not washed down the sewer.

Figure 1 – CO2+ Cleaning Process

The objective of this test study is to identify if the CO2+ cleaning system which provides superior cleaning and decontamination results can also be effective from removal of PFAS compounds which are present on the firefighter gear and generated at firefighter incidents.

The approach for this study is to evaluate the effectiveness of CO_2 cleaning for PFAS removal is to rely on the existing cleaning protocols specified in the NFPA 1851 standard combined with incorporation of PFAS analytical testing methodologies using CO_2-based cleaning process technology developed by the applicant. The NFPA is an international nonprofit organization devoted to eliminating death, injury, property, and economic loss due to fire, electrical and related hazards. The NFPA 1851 Standard specifies test protocols for evaluation of decontamination efficiencies for specified metals and SVOCs and defines test load characteristics for the decontamination efficiency evaluations. This study used NFPA-1851 testing protocols to conduct the PFAS decontamination test evaluations. The use of this standard serves as a test baseline of which will be understood by persons in this field.

EXPERIMENTAL METHODS: PFAS testing using the CO2+ cleaning system largely though not identically followed the protocols identified in NFPA-1851. Test swatches were prepared, surrogate garments were used, 40 lb ballast was used.

As there are not 1851 standards detailing PFAS analysis and testing protocols and modified the doping and analytical procedures following protocols used in other EPA test methods:

- Perfluoroalkyl Substances were analyzed using LC/MS/MS following ASTM D7968 (M);
- Legend Technical Services (LTS) of St. Paul, MN was used as the analytical lab for these tests;
- Test swatches were cut to 3" x 6" following SVOC test protocols of 1851;
- Following NFPA protocols, swatches were doped with 200 ppm PFAS solution by applying 300 µL to the swatch, resulting in a doping mass of about 6000 ng/swatch PFAS to the swatch;
- PFAS Analytes were doped on the test swatches: Perfluoro-n-octanoic Acid (PFOA) – 61,000 ng/g wet, Perfluoro-n-tetradecanoic Acid (PFTeDA) – 62,000 ng/g wet, Perfluoro-1-butanesulfonate (PFBS) – 52,000 ng/g wet, Perfluoro-1-octanesulfonate (PFOS) – 77,000 ng/g wet.

The CO2+ cleaning system located in the ETD facility in Eagan, MN was used for these tests. The system was programmed for an 18-minute wash cycle using the 'Outer Shell' program, which has a cycle duration of about 70 minutes, which is characterized in Figure 1 above. The test swatches were inserted in the surrogate garments using procedures specified in NFPA 1851. At the completion of the cleaning cycle, the ballast and test garments were removed from the machine, the test swatches were collected and inserted into clean transfer tubes, which were subsequently returned to the LTS for analysis. Two tests were conducted, one on 29 January 2021 and a follow-up test on 26 February 2021.

TEST RESULTS AND DISCUSSION: The test results shown in Table 1 indicate effective PFAS removal for four PFAS analytes. It is noteworthy that all tests showed similar removal efficiencies among the analytes examined, despite a full month between the PFAS tests. The average PFAS removal of these analytes was about 84%.

Table 1 – PFAS Test Results

PFAS Analyte	PFAS Test 1 - 29Jan21	PFAS Test 2 - 26Feb21
Perfluoro-n-octanoic Acid (PFOA)	88.2%	86.3%
Perfluoro-n-tetradecanoic Acid (PFTeDA)	97.2%	98.5%
Perfluoro-1-butanesulfonate (PFBS)	61.1%	59.6%
Perfluoro-1-octanesulfonate (PFOS)	91.2%	91.3%
Average	84.4%	83.9%

Based on a review of the recent paper by Young et al [1], they report total PFAS mass loading from wipe tests ranging from 1.28 to 84.5 µg/swatch using at 3"x3" swatch and wipe solvent is IPA (equivalent to 0.02 – 1.45 ng/cm^2). Based on data provided by Laitnen et al. [2], they report sum of 4 PFAS totaling about 0.25 ng from a sample piece of turnout gear - 4 cm^2 (equivalent to 0.06 ng/cm^2). For this study, we followed the NFPA specification of doping the swatch with 200 ppm PFAS solution by applying 300 µL to the swatch, yielding a loading of about 60,000 (range from 29,000 – 77,000) ng/swatch PFAS. The swatch dimensions were 3"x6" (116 cm^2). Hence the nominal loading on the test swatches was substantially greater than those identified in the literature: about 60,000 ng/swatch / (116 cm^2/swatch) = 517 ng/cm^2. The PFAS loading mass value is substantially more (about 500x) than observed in the literature cited above. Subsequent tests should be conducted using a concentration of about 1 ppm PFAS, which will give us a nominal PFAS mass of 150-300 ng/swatch or about 2.6 ng/cm^2. Further, subsequent testing should employ the smaller NFPA 1"x2".

Examining these data from the perspective of PFAS removal capability of the CO2+ cleaning system, these data demonstrate that approximately 84% of the nominal 60,000 ng/swatch (517 ng/cm^2) was removed, or about 434 ng/cm^2, indicating that the CO2 + chemistry should have the carrying chemistry to capture most if not all the PFAS on these substrates assuming typical loading rates. However, this hypothesis will need to be verified by further testing.

References

1. Young, A.S, E.H Sparer-Fine, H.M. Pickard, E.M. Sunderland, G.F. Peaslee and J.G. Allen; Per- and polyfluoroalkyl substances (PFAS) and total fluorine in fire station dust; Journal of Exposure Science & Environmental Epidemiology, Received: 24 June 2020 / Revised: 30 November 2020 / accepted: 6 January 2021; https://doi.org/10.1038/s41370-021-00288-7.
2. Laitinen J, Tuomi T, Vainiotalo S, Laaja T, Rantio T,Parshintsev E, Kiviranta H, Koponen J, Pyrstöjärvi P,Kemmeren M, Heus R.; Contamination and decontamination of firefighting garments –Laboratory tests, Finnish Institute of Occupation Health, 8/28/18.