

Testing of clothing for the protection of firefighters against exposure to polycyclic aromatic hydrocarbons in fire smoke



Commissioned by:

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1. Summary

The present report presents measurements carried out to determine and compare the protection against exposure to polycyclic aromatic hydrocarbons (PAHs) in fire smoke obtained using two different constellations of protective clothing for firefighters. On the one hand, protective clothing of the standard type has been examined: Both underwear and fire suit are here of the standard type that is normally used by firefighters in Sweden today in connection with smoke diving. In addition, protective clothing with reinforced protection has been examined: The under wear has here been replaced with an undergarment made of an adsorptive material. The outerwear is still the fire suit that is normally used today, i.e. identical to the fire suit used in the experiments with standard protective clothing.

In summary, the results clearly show that the constellation with the adsorptive undergarment provides a marked reduction in the amount of PAH that penetrates the protective clothing to the skin compared to the constellation without adsorptive underwear. The standard clothing set up reduced the total amount of PAHs to an average of one-fifteenth (1/15) of the amount of PAHs in the smoke. The reinforced clothing, with adsorptive underwear, typically reduced the amount of PAH to less than one thousandth (1/1000) when the adsorptive underwear was new. As adsorptive underwear has aged through use in ten smoke dives with intermediate washes, the reduction of PAHs decreased. The protective clothing then reduced the amount of PAH to just under one six of a hundredth (1/600). The values in previous part means that the different constellations have protection factors as follows:

Constellation of clothing	Protection factor
Clothing of standard type	15
Clothing with new adsorptive underwear	1000
Clothing with adsorptive underwear used and washed 10 times	600

The results indicate that more PAH penetrates under the adsorptive hood than under the adsorptive underwear in general. This may be due to contaminated air leaking under the hood in connection with the firefighter's movements. However, the adsorptive hood provided on average about three times better protection than the standard hood did.





2. Background

Firefighters who are exposed to hazardous substances in fire smoke are at greater risk than the general population of developing cancer. In this context, polycyclic aromatic hydrocarbons (PAHs) are particularly important as several of the substances included in this group of substances are documented to be carcinogenic. The exposure occurs when PAH penetrates the firefighters' protective clothing and is deposited on the skin.

With the aim of finding methods to protect firefighters from this work environment risk, the Firefighters' Cancer Fund has commissioned CIT Energy Management to study the ability of alternative protective clothing to prevent the penetration of PAHs.

The assignment has been carried out through measurements, partly on a small scale on test pieces of protective clothing, partly on a full scale in connection with exercises where firefighters carried out smoke dives. The measurements were carried out at Guttasjön's fire drill site in collaboration with staff from Södra Älvsborgs Räddningstjänst-förbund. Measurements were made partly on the standard clothing used in the rescue service today, and partly on a reinforced clothing system, where the standard underwear was replaced with a new underwear made of a so-called adsorptive textile, containing a layer of activated carbon, as well as a layer with particle filter.

The tests were performed on three occasions during 2019 and 2020. The work was performed by the following people:

- Lars Ekberg, Adj. Prof., CIT Energy Management AB, Göteborg. (www.enerma.se).
- Sarka Langer, Adj. Prof., IVL Svenska Miljöinstitutet, Göteborg (<u>www.ivl.se</u>).
- Bo Strandberg, Docent, Arbets- och Miljömedicin, Lunds Universitet (https://www.lu.se/lucat/group/v1000552)

3. Aim

The study aims to determine and compare the protection against PAH exposure in fire smoke obtained when using two different constellations of protective clothing for firefighters. The goals are that the survey result should:

- contribute to increased knowledge and awareness of the work environment risk that exposure to PAHs in fire smoke entails for firefighters
- point to a concrete opportunity to significantly reduce the risk by using protective clothing that effectively reduces the penetration of PAHs.

4. Tested materials

The tested materials where of two types:

- 1. **Protective clothing of standard type**: Both undergarments and fire suit are of the standard type that is normally used by firefighters in Sweden today in connection with smoke diving.
- 2. **Protective clothing with reinforced protection**: The underwear has been replaced here with an underwear made of an adsorptive material. The outerwear is still the fire suit that is normally used today, i.e. identical to the fire suit used in the experiments with standard protective clothing.





Tests were carried out with new, ie previously unused, clothing materials as well as with clothes, both fire suit and undergarment, that had been used before, in this case 10 smoke diving with intermediate launderings. The adsorptive undergarment was provided by CPP Garments AB (CPP).

5. Test method

This section describes in turn:

- Test rig for testing textile samples
- Sampling in connection with smoke diving in full scale
- Sampling of PAH
- · Chemical analysis of PAH

5.1 Test rig for testing textile samples

- Samples of the adsorptive textile were provided by CPP Garments. Samples of the protective clothing were cut from new fire suits and undergarments.
- A fire situation was simulated in a steel container by burning wood-based material. Photos in Appendix 1 illustrate the test setup.
- The tested textile samples were exposed to fire smoke through 200x200 mm openings fitted with 300x300 mm steel shutters.
- PAHs were sampled with polyurethane foam (PUF) samplers according to the method described in a separate section below.
- The textile samples were applied together with PUF samplers on the steel cover according to the sketch in Figure 1.
- The temperature was measured partly on the inside / fire side, partly on the outside / skin side, with thermo-elements type K.

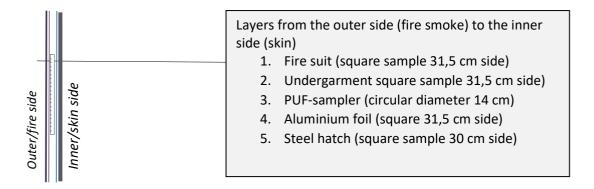


Figure 1. Sketch and photo illustrating how PUF samplers and textiles were applied to the steel hatch in connection with testing of textile samples. Photos showing the event can be found in Appendix 1.





5.2 Tests in conjunction with full scale smoke diving

- A fire was simulated in a building intended for smoke diving exercises. Appendix 2 contains photos of the current training site.
- Smoke divers performed smoke dives in pairs, one of the smoke divers wearing standard
 protective clothing, and the other smoke diver wearing the reinforced clothing system, as
 described in a separate section above.
- PAHs were sampled with polyurethane foam samplers (same type of PUF as for textile testing) according to the method described in a separate section below.
- The PUF samples were applied directly to the firefighters' skin, thighs, chest, upper arms and neck
- The temperature was measured with a stand-alone temperature logger model TinyTag which
 was placed in the alarm place's pockets, partly at a low level (leg pocket), partly at a high level
 (chest pocket).
- Each smoke dive lasted for 25 minutes. Some exercises included only one such a smoke dive, while other exercises included two 25 minutes smoke dives with an intermediate break of 25 minutes.

5.3 Sampling of PAH

- The majority of PAH samples were taken with passive polyurethane foam (PUF) samplers. The samplers are circular with a diameter of 14 cm.
- The PUF samplers were applied to the skin side, ie inside the innermost layer of clothing (the underwear).
 - O When testing textile samples, the PUF sampler was placed on an aluminium foil which in turn was applied to the steel door according to Figure 1. A sample piece of the underwear textile placed on the PUF and finally a sample piece of the fire suit textile was applied. The edges of the door / textile package were sealed with aluminium tape. When the door was closed, the fire suit textile was exposed directly to the fire smoke.
 - During the full-scale smoke diving exercises, the PUF samplers were applied directly to the firefighters' skin, thighs, chest, upper arms and neck. They were held in place with surgical tape.
- A PUF sampler was applied to the outside of the clothing directly exposed to the highly concentrated fire smoke, both in the case of testing textile samples and in the case of full-scale smoke diving.
- The samplers were applied immediately before each exposure and removed immediately after exposure.
- The samplers were wrapped in aluminium foil and transported without delay to the laboratory for chemical analysis.

5.4 Chemical analysis of PAH

After sampling, PAH was extracted from the samplers with *Accelerated Solvent Extraction* (ASE 350) equipment. The sample was then purified from interferences using a column of silica gel. Finally, analysis was performed with a gas chromatograph with mass spectrometer (GC / MS).





The results are expressed as the sum of 32 individual polycyclic aromatic hydrocarbons. This value is called Total-PAH. Individual substances were also identified and quantified (including the 16 US EPA PAHs). The quantification was expressed as the amount of PAH in the unit nanogram per sampler (ng / sample).

To assess the clothes' ability to prevent the penetration of PAHs, the result is reported as the amount of PAHs on the "skin side" (under the clothes) in relation to the amount of PAHs on the "outside" (in the fire smoke). This measure is referred to in the report as "penetration" and it indicates the proportion of the amount of PAH in the fire smoke that penetrates the clothing layers. The inverse of the numerical value of the penetration is called the "protection factor". For example, the protection factor 1000 means that the amount of PAH under the clothes, on the skin side, is one thousandth (1/1000) of the amount of PAH in the surrounding fire smoke.

6. Results from testing of textile samples

Figure 2 and Figure 3 show the results of two rounds of measurements on test pieces of textiles. The two rounds of measurement were performed in an identical manner. In both cases, textile samples from a standard garments as well as textile samples from reinforced protection undergarment of adsorptive textile were tested.

The results from the two rounds of measurement are consistent and show that on average 10% of the total amount of PAHs in the fire smoke penetrated the protective clothing of standard type. The corresponding figures for the reinforced protection (adsorptive) materials is 0.1%.

The figures above mean that the protection factor for the reinforced protection with the adsorptive material was about 100 times higher than the protection factor for the standard material.

Both Figure 2 and Figure 3 show that the penetration of PAH was not affected by the exposure time to any measurable extent.

The reinforced protection (adsorptive) material used in all the smoke diving exercises was made of the same material as the tested material mentioned above.





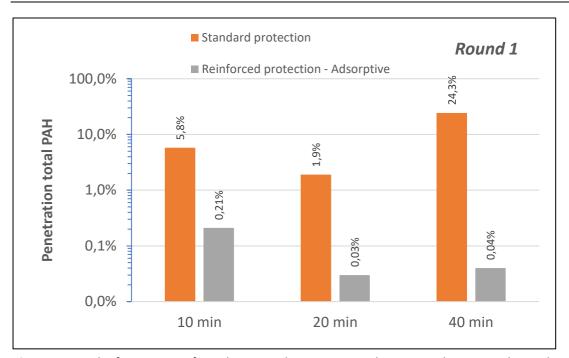


Figure 2. Results from a test of textiles carried out in September 2020. The material samples were exposed to fire smoke for three different times, 10 minutes, 20 minutes and 40 minutes. The result is expressed as the amount of PAH on the inside / skin side in relation to the amount of PAH in the fire smoke.

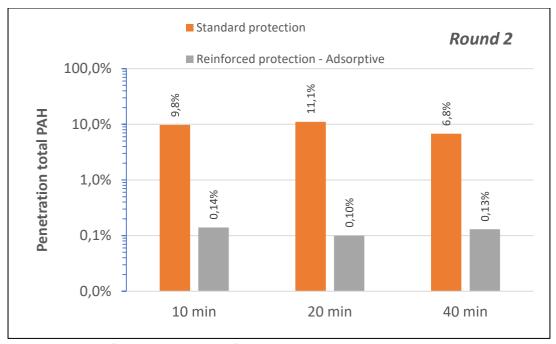


Figure 3. Results from a second test of textiles carried out in September 2020. The material samples were exposed to fire smoke for three different times, 10 minutes, 20 minutes and 40 minutes. The result is expressed as the amount of PAH on the inside / skin side in relation to the amount of PAH in the fire smoke.





7. Results from smoke diving

Figure 4 shows results from a smoke diving exercise carried out in September 2020. The smoke diving lasted for 25 minutes with new, previously unused, clothes. The result is expressed as the penetration of the total PAH, ie the total amount of PAH on the inside / skin side in relation to the total amount of PAH in the fire smoke on the outside of the clothes.

The figure shows that between 1% and 12% of the total amount of PAH penetrated the standard protective clothing. These figures mean that the amount of PAH under the clothes, on the skin side, was between 1/89 and 1/8 of the amount of PAH in the surrounding fire smoke. Thus, the result means that the protection factor for the standard clothes varied between 8 and 89.

For the clothes with reinforced protection, the penetration was instead between 0.02% and 0.04%. The <u>protection factor for the reinforced protection thus varied between 2500 and 5000</u>. The adsorptive base in this experiment was in the form of an entire overall with a separate hood.

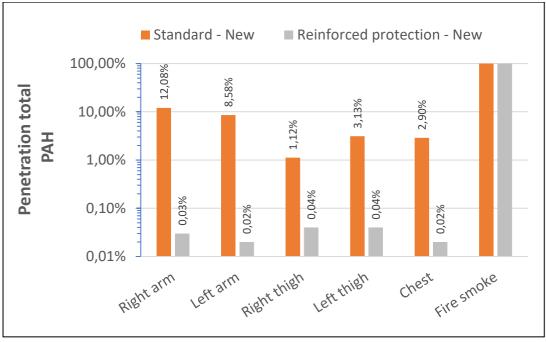


Figure 4. Results from a smoke diving exercise carried out in September 2020. The smoke diving lasted for 25 minutes with <u>new previously unused clothes</u>. The result is expressed as the amount of PAH on the inside / skin side in relation to the amount of PAH in the fire smoke on the outside of the clothes.

In December 2020, new smoke diving attempts were carried out, both with new protective clothing and with protective clothing used previously. The used bases of adsorptive material were the same as those used in the experiments in September (Figure 4), ie a whole overall with a separate hood. Before the experiments began in December, however, the previously used (in September) protective clothing had been used on ten different occasions, including 25-minute smoke-diving exercises, and washed in between.



In addition, new adsorptive undergarments were tested that were two-piece (trousers and jacket) with a separate hood. They were made of a textile that was of the same type as the previously used and tested underwear in the form of complete overalls.

Figure 5 shows the results from a smoke diving exercise with previously used and washed underwear and fire suit. In both cases, the exercise included two 25-minute smoke dives with an intermediate break of 25 minutes. As can be seen from the figure, between 6% and 8% of the total amount of PAH penetrated through the previously used standard protective clothing. This means that the standard clothing in this experiment showed a protection factor that varied between 12 and 16.

For the clothes with reinforced protection (to the same extent used and washed), the penetration was instead between 0.10% and 1.43%, which means that the protection factor in this case varied between 70 and 1000. Just as in the case of new underwear (reported in Figure 7 below) the lower value of the protection factor for samplers placed on the neck was observed. If the sample in the neck is excluded, the lowest value of the protection factor is 770.

Figure 6 shows the results of another smoke diving exercise with previously used protective clothing. In this case, however, the exercise included only a smoke dive of 25 minutes. The protection factor for the standard clothing varied in this case within the range 28 - 67. For the clothing with reinforced protection, the protection factor varied instead in the range 17 - 1111. Again, it was the sample in the neck that showed the lowest protection factor. It is possible that the hood wasn't enough covered inside the fire suit which could have led to "a gap" when the firefighter moved the head. This can explain the lower protection factor in the neck. It is also possible that the hood was too big which could have led to poor fitting. If the sample in the neck is excluded, the lowest value is the protection factor 500.

The measured values in Figures 5 and 6 suggest that more PAH penetrated the standard clothing at two repeated 25-minute smoke dives compared to a single 25-minute smoke dive. However, there is no such difference for the clothes with reinforced protection.

By comparing Figure 4 and Figure 6, an indication is obtained of how the protective ability of the clothes changes when the adsorptive undergarment ages. Both figures report data for the undivided adsorptive overall in connection with a single 25-minute smoke dive. Figure 4 applies to the case of new underwear and Figure 6 to the case of underwear that has been used and washed ten times.

For the new clothes, the measurements showed a total penetration of PAH in the range 0.02% - 0.04% with an average value of 0.03%. When the same overall was used ten times, the measurements instead showed a penetration in the range 0.09% - 0.2% of an average of 0.15% (which corresponds to a protection factor of 660). Sampling in the neck was done only in the case of the clothes used, so this value was excluded from the comparison. In summary, the measurement results indicate that the adsorptive clothes used offered a lower protection factor than the new ones.

However, the protection factor for the adsorptive clothes used was significantly higher than the protection factor for the standard clothes.





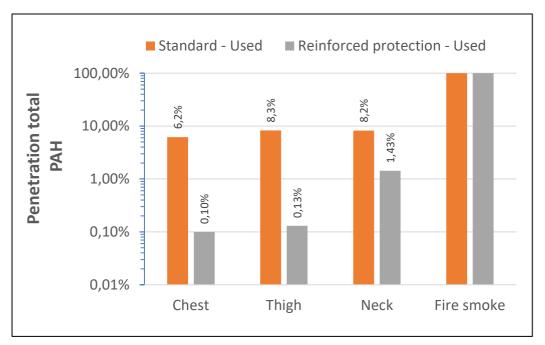


Figure 5. Results from a smoke diving exercise carried out in December 2020. The exercise included two smoke dives for 25 minutes each with an intermediate break of 25 minutes. <u>Both fire suit and underwear had been used and washed 10 times before.</u> The adsorptive underwear was a one-piece (trousers and jacket) overall. The result is expressed as the amount of PAH on the inside / skin side in relation to the amount of PAH in the fire smoke on the outside of the clothes.

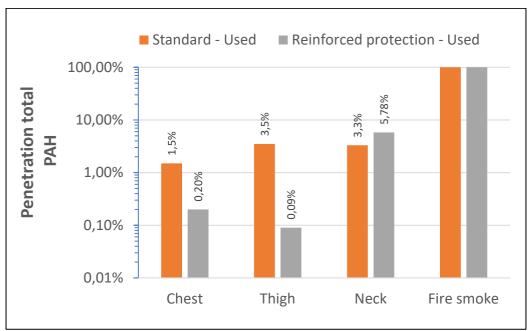


Figure 6. Results from a smoke diving exercise carried out in December 2020. The exercise included a single smoke dive of 25 minutes. <u>Both fire suit and underwear had been used and washed 10 times before.</u> The adsorptive underwear was a one-piece (trousers and jacket) overall. The result is expressed as the amount of PAH on the inside / skin side in relation to the amount of PAH in the fire smoke on the outside of the clothes.





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Figure 7 shows the results from a smoke diving exercise in December 2020 with new, previously unused, two-part undergarment (but used fire suit). As can be seen from the figure, between 6% and 16% of the total amount of PAH penetrated the protective clothing of the standard type (new underwear and used fire suit). These figures mean that this clothing combination showed a protection factor that varied between 6 and 16.

For the clothes with reinforced (adsorptive) protection, the penetration was instead between 0.08% and 0.29%, which means that the protection factor in this case varied between 345 and 1250. The lower value of the protection factor was observed for the sampling on the neck. It is possible that this sampling site / body part was contaminated by air leakage under the hood in connection with the firefighter's head movements. It is also possible that the hood was too big which can have led to increased "leakage".

Figure 8 compares the results for two smoke divers who were both dressed in a new adsorptive two-piece undergarment; one had a previously used fire suit and the other a new unused fire suit. For the smoke diver with a new fire suit, the protection factor was in the range 175 - 1111, while for the smoke diver with a previously used fire suit it was 345 - 1250. As with previously reported results, the lowest values of the protection factor for the sampler in the neck were observed.

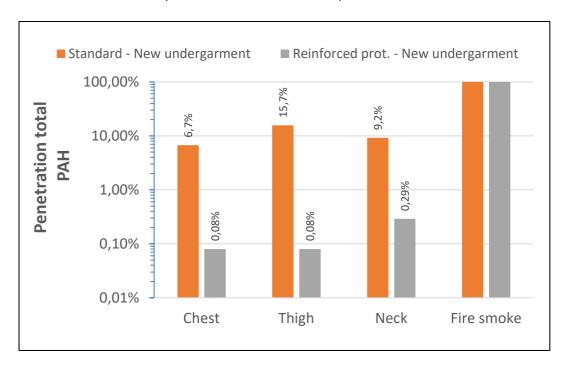


Figure 7. Results from a smoke diving exercise carried out in December 2020. The exercise included two smoke dives for 25 minutes each with an intermediate break of 25 minutes. The fire suit had been used before while the underwear (two-piece) was new. The result is expressed as the amount of PAH on the inside / skin side in relation to the amount of PAH in the fire smoke on the outside of the clothes.





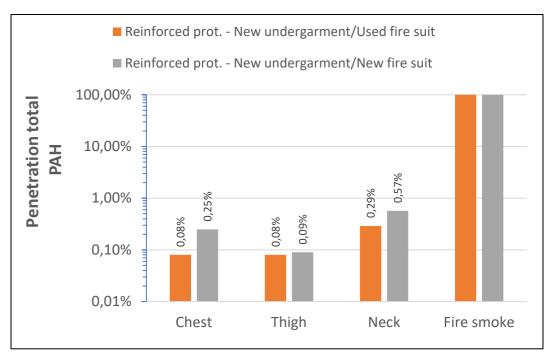


Figure 8. Results from smoke dives carried out in December 2020. The exercise included two smoke dives for 25 minutes each with an intermediate break of 25 minutes. Both smoke divers were dressed in <u>new adsorptive two-piece underwear</u>. One smoke diver had a previously <u>used fire suit</u> and the other a <u>new unused fire suit</u>. The result is expressed as the amount of PAH on the inside / skin side in relation to the amount of PAH in the fire smoke on the outside of the clothes. The result for the smoke diver with used turnout gear has already been reported in Figure 7 above.

8. Summary of all smoke diving tests

The measurement results from the smoke diving exercises are summarized in their entirety in Table 1 and in Figure 9. As can be seen from the table, the standard clothing showed just over 6% penetration of PAH, both as an average and as a median value. The results were pretty well collected; 25% of the samples showed less than about 3% penetration and 25% of the samples showed more than about 9% penetration (25% -in and 75% -il, respectively).

The measurement results for the clothes reinforced with adsorptive undergarments showed greater spread. The penetration of PAH was in that case about 0.5% expressed as average, but only 0.09% expressed as median. This is because the samples taken in the neck under the adsorptive hood in most cases showed significantly higher penetration than other samples under the adsorptive underwear (on thighs, arms and chest). The mean value of PAH penetration for all samples excluding those in the neck was approximately 0.09%. This value corresponds to a protection factor of about 1100.



Table 1. Summary of all smoke diving attempts with standard protective clothing and protective clothing with underwear for reinforced protection. The information in the table is also presented for the sake of clarity in Figure 9.

	Standa	Standard clothing		d protection rptive nent	Protection factor's
Measures	Pene-		Pene-		Reinforced/standard
	tration	Protection	tration	Protection	
	total PAH	factor	total PAH	factor	
Max	15,7%	6	5,78%	17	3
75%-il	8,7%	11	0,25%	400	36
Average	6,5%	15	0,54%	185	12
Median	6,4%	15	0,09%	1100	73
25%-il	3,1%	32	0,04%	2500	78
Min	1,1%	91	0,02%	5000	55

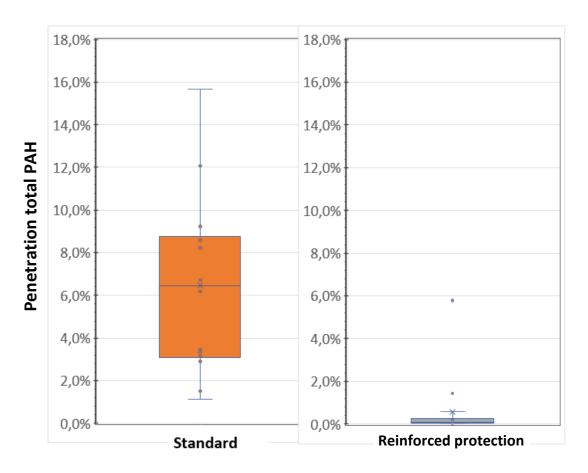


Figure 9. Box and whisker chart showing the average PAH penetration average, median, minimum and maximum values for all samples of standard protective clothing and protective clothing with reinforced underwear. The values are also given in Table 1.





In summary, the measurements carried out show the following:

- The total amount of PAH on the skin side, inside the standard protective clothing tested, was on average about 6% of the total amount of PAH in the fire smoke. This corresponds to just over a fifteen-fold reduction in the amount of PAH (protection factor 15).
- The total amount of PAH on the skin side, inside the protective clothing reinforcerd with an adsorptive undergarment, was for most of the samples less than 0.1% of the total amount of PAH in the fire smoke. This corresponds to just over a thousand-fold reduction in the amount of PAH (protection factor 1000).
- The total amount of PAHs on firefighters' necks, under the hood of standard clothing, was on average 7% of the total amount of PAHs in the fire smoke.
- The total amount of PAHs on the necks of firefighters, under the adsorptive hood of reinforced clothing, was on average 2% of the total amount of PAHs in the smoke. This is less than a third of the equivalent value of the standard clothing hood. However, the samples under the adsorptive hood showed greater penetration than other samples under the adsorptive base (samples on thighs, arms and chest).
- The measurement results thus indicate that the reinforced clothing system provided poorer
 protection of the neck than of other body parts where PAH was sampled. It is not clear what it is
 due to, but one explanation could be that air leakage occurs under the hood when the
 firefighter moves the head.
- The measurement results indicate a deterioration of the protection factor of the adsorptive clothes after ten uses with intermediate washes. For the undivided adsorptive overall, the measurements showed a total penetration of PAH of on average 0.03% when new. When the same overall was used ten times, the measurements instead showed a penetration of an average of 0.15%. These figures mean that the protection factor fell from 3300 to 660.



Appendix 1. Photos of test set up for testing of textile samples



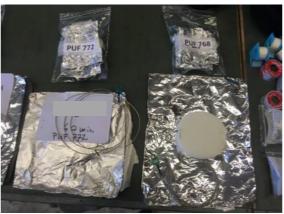




Figure B1.1 Package with PUF-samplers and textiles prepared for testing in test rig.









Figure B1.2 Test rig - a steel container - prepared for testing of textiles. The photos on top show the 5 hatches where the material samples were applied.









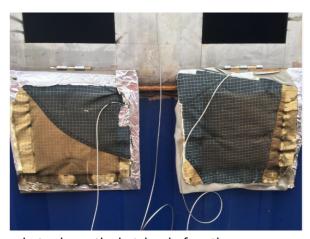


Figure B1.3 The test rig seen from outside. The left top photo shows the hatches before the material samples were applied. The top right photo shows the material samples when they have been applied for the test. The two lower photos show the material samples after exposure of fire smoke.



Appendix 2. Photos from the smoke diving exercises

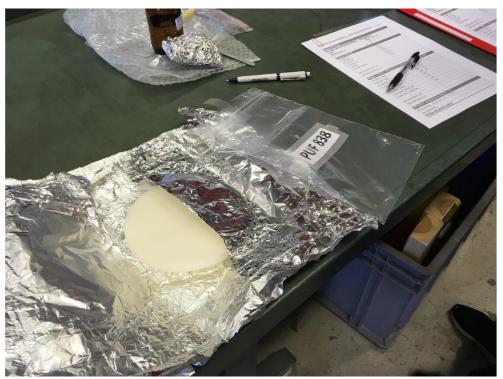


Figure B2.1 PUF-sampler in aluminium foil.



Figure B2.2 PUF-sampler applied on arm.







Figure B2.3 Firefighter dressed in adsorptive undergarment.



Figure B2.4 Firefighters in fire suits without complete fire hoods. The two firefighters to the left have adsorptive undergarments including adsorptive hood.





Figure B2.5 Firefighters in fire suits ready for starting the tests.





Figure B2.6 The place for the exercises during smoke diving.



Figure B2.7 Firefighters after smoke diving.





Appendix 3. Identified and quantified individual PAHs

naphthalene

2-methylnaphthalene

1-methylnaphthalene

biphenyl

2,3-dimethylnaphthalene

acenaphthylene

acenaphthene

2,3,5-trimethylnaphthalene

fluorene

1-methylfluorene

phenanthrene

anthracene

2-methylphenanthrene

3-methylphenanthrene

1-methylphenanthrene

1-methylanthracene

2-phenylnaphthalene

fluoranthene

pyrene

1-methylfluoranthene

retene

1-methylpyrene

benzo(a)anthracene

chrysene

2-methylchrysene

5-methylchrysene

benzo(b)fluoranthene

benzo(k)fluoranthene

benzo(e)pyrene

benzo(a)pyrene

perylene

indeno(1,2,3-c,d)pyrene

dibenzo(a,h)anthracene

benzo(g,h,i)perylene

coronene

