ENSURING OF INDIVIDUAL DECONTAMINATION OF HAZARDOUS CHEMICALS IN THE FIRE RESCUE SERVICE OF THE CZECH REPUBLIC. PART 3: EVALUATION OF USER PROPERTIES OF SELECTED MEANS AND PROCEDURES

Tomas CAPOUN, Jana KRYKORKOVA
tomas.capoun@ioolb.izscr.cz

Abstract

In order to equip regional FRS units with effective means of individual decontamination, we have drawn a comparison of some procedures and means (decontamination by sorbent, decontamination glove and cloth, two-chamber device, wiping with alcohol). We have evaluated both economic aspect and some user parameters such as decontamination of heavily accessible places and vertical areas, need of water for rinsing, waste risks and waste disposal.

Key words

Chemical warfare agent, warfare poisonous substance, individual decontamination, decontamination glove, decontamination cloth, Desprach, waste risks, waste disposal.

INTRODUCTION

The main objective of our engagement was to propose a method of ensuring effective individual decontamination for regional FRS units. The concept of individual decontamination represents the decontamination procedure of contaminated parts of the body surface, individual protection equipment and material equipment imminently after the contamination. This procedure is performed by self-support or by mutual assistance with the application of ordered or improvised means [1, 2]. It is a specifically important anti-chemical measure against the consequences of an uncontrolled leak of chemical warfare agents and other hazardous substances into the environment and capable to minimize substantially health and irreversible losses [3-5]. Currently, this is not, either technically or methodically ensured both at regional FRS units [1, 2] and other sections of the Integrated Rescue System [5].

With regard to the main objective we summarized the theoretical knowledge of available means and procedures of individual decontamination [1, 2]. With selected representatives of various principles we assessed the decontamination effectiveness during the decontamination of test surfaces contaminated by the agent VX, sulfide yperite, o-cresol and acrylonitrile [2, 6]. Concurrently we discovered a significant difference in decontamination effectiveness of tested means and procedures regarding individual contaminants. The only procedure by which we reached the reduction of surface contamination under the value of permissible residual contamination, was wiping the surface with ethanol.

However, the decontamination is not only the issue of the decontamination effectiveness. It is also the issue of other parameters of tested means such as user properties, safety of users, costs etc. Specified parameters were compared for the following means and procedures whose decontamination effectiveness was tested in the previous part [6]:

- decontamination nano-sorbent FAST-ACT in a plastic application bottle,
- decontamination glove FAST-ACT,

- decontamination cloth RSDL,
- prototype of Czech decontamination cloth,
- prototype of two-chamber applicator of foam Hvezda,
- means DESPRACH in plastic bottle - the kit ZPJ-80,
- procedure of wiping contaminated surface with ethanol.

The above specified means and procedures were described in a previous volume [1].

DECONTAMINATION OF HEAVILY ACCESSIBLE PLACES AND VERTICAL AREAS

Regarding the character of individual decontamination, it is obvious that it includes also the decontamination of minor material means which are variably dissected with heavily accessible places such as internal corners, grooves etc. The decontamination of these places after the application of verified means and procedures is not a problem. Loose sorbent can be, especially in the application form as means DESPRACH, applied practically everywhere. Also the utilization of decontamination cloths, foam and blanks dipped in alcohol is nowise spatially limited. The exception is a decontamination glove with which it is much more convenient to clean straight larger areas, whilst the contact with heavily accessible places is limited.

The possibility of the decontamination of vertical areas and internal upper areas is supposed to be a matter of course in individual decontamination procedures. Means based on decontamination solutions either on a chemical principle (decontamination cloths, foam applicator or on a physical principle (wiping with alcohol) fully comply. The problems occur in case of the application of sorbents. The means DESPRACH in the kit ZPJ-80 includes a tampon on which the sorbent is sprinkled and then a vertical place is wiped. This procedure is real despite the fact that it is less effective than in case of a horizontal place. The bottle with nano-sorbent FAST-ACT, basic version, is not equipped with such tampon so the decontamination of vertical areas is not possible. Practically it means to apply some improvised means for wiping, nevertheless, the instructions [7] for sorbent do not mention this option since only sprinkling of a contaminated place is supposed.

NEED OF WATER FOR RINSING

The necessity to rinse a decontaminated surface with water is a significant parameter due to the fact that water for an assisting unit might not be available around a contaminated area.

Regarding this fact it is very effective to apply sorbents (decontamination gloves, solid sorbents DESPRACH and FAST-ACT) or wiping with alcohol since there is not need of water.

The application of foam Hvezda also requires to rinse the reaction mixture on the surface with water because the aggressive residues might have a negative effect on surfaces.

Somewhat unclear is the need of water after the application of decontamination cloths. The manual says that the surface is rinsed with water after 2 minutes of the exposure to decontamination solution “as long as the water is available“. At the same time it warns that the decontamination solution might have irritating effects. Definitely it would be necessary to rinse the skin and technical surfaces as well due to a potential contact of an uncovered part of the skin with a decontaminated place.

The necessity to rinse the surface with water after the application of the means of individual decontamination is narrowly connected with another significant user parameter which is the possibility of decontamination in case of the frost. The procedures requiring the application of water cannot be used in case of very low temperatures. On the contrary, separate tests proved that the temperatures around - 18 °C do not reduce the decontamination effects of sorbents and alcohols [8].

ECONOMIC COMPARISON

Within the frame of this work we mutually compared the price of commercial means, means DESPRACH which has not been produced any longer and some prototypes for which the price has not been fixed yet. Therefore the economic evaluation is very difficult. Some prices are specified in table 1. These prices are for 1 means without any bulk discount.

In any case, at the FRS CR the price should not play a major role but other related parameters should be taken into account such as determining economic demandingness of a given means i.e.:

- lifetime, i.e. the frequency of necessary replacement,
- repeatability of the application of one means, i.e. the question of „disposability,
- total area which can be decontaminated by a given means.

Also these parameters are summarized in Table 1.

WASTE RISKS AND WASTE DISPOSAL

The Importance of Waste Analysis

When applying the means or procedures of individual decontamination, we cannot omit the issue of waste risks. Procedures based on a physical principle mostly only remove the contaminant from the surface which results in highly contaminated waste. In case of the application of a decontamination cloth and sorbent FAST-ACT, the decomposition of a chemical warfare agent is declared [1, 2, 7]. For the objective evaluation of waste risks after the decontamination by verified procedures we carried out the analysis of the waste by the method of gas chromatography with mass detector (GC/MS) [2].

After the completion of decontamination described in a previous paper [6], the applied means were hermetically sealed in a vial and analyzed by GC/MS method, technique head-space with the solid phase micro-extraction (SPME) [9]. For SPME we used the Carboxen/Polydimethylsiloxan fiber.

The vial with the sample of applied decontamination means was inserted in a water bath heated to 80 °C and left here for 30 minutes. Then the septum was pierced by the SPME holder and the fiber was ejected. Beforehand this fiber was conditioned at the temperature of 300 °C for one hour. The sorption time amounted to 5 minutes without ejecting the vial from the thermostat. After this time the fiber was inserted and after the ejection of the holder from the vial applied into the device GC/MS [9].

The analyses were carried out on a gas chromatograph with mass detector GC/MSD 7890/5975C (Agilent Technologies, Inc., Wilmington, USA) with column HP-5MS (Agilent), length 30 m, ø 250 µm, phase 0,25 µm.

Parameters of measurements:

- Bearing gas He 1,2 ml/min,

- T Inlet 290 ºC,
- T interface GC/MSD 290 °C,
- Scan range 35-800 amu,
- Split 10:1,
- GC program: 40 ºC – 2 min, from 40 ºC to 280 ºC dT/dt 10 ºC/min, 280 ºC–10 min.

The Waste Generated after the Decontamination of VX Agent

After the decontamination of VX agent by sorbent DESPRACH or by the decontamination glove FAST-ACT, the waste contains high concentrations of the VX agent as it is obvious from the chromatogram in Fig. 1 where the VX agent peaks at the retention time 19.9 min. The agent VX is also present in the waste after the wiping with ethanol (Fig. 5). Evidently, the waste represents high risk of inhalation intoxication. Fig. 1 also includes the chromatograms of waste after the application of a decontamination cloth RSDL and sorbent FAST-ACT which take place in the area about 20 minutes practically along a baseline. For illustration, the detail of a chromatogram in Fig. 1 is demonstrated in the time range around the peak of VX agent in Fig. 2. It is obvious that the contaminant was due to the effect of both RSDL solution and sorbent FAST-ACT completely decomposed. The conclusions for cloth RSDL is valid in a full range also for the Czech prototype of this means. Fig. 1 demonstrates also some decomposition products of the agent VX.

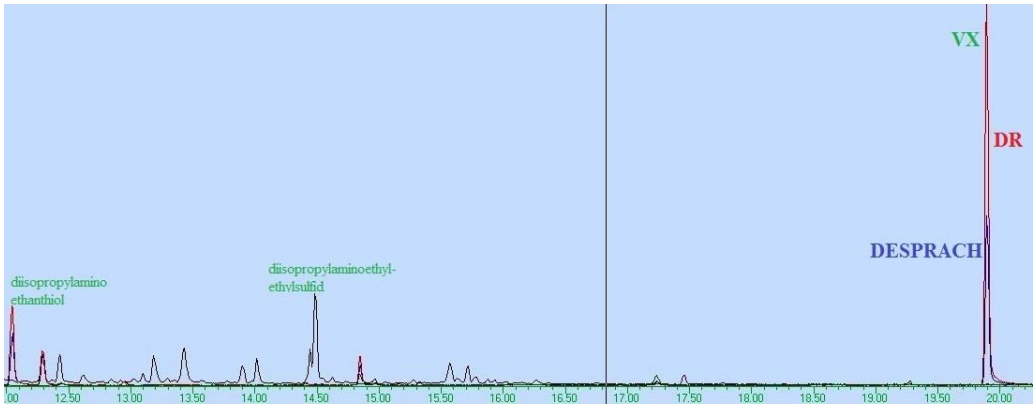

Fig. 1
Chromatogram of waste after the decontamination of VX agent by sorbent DESPRACH and a decontamination glove (DR)

The specified chromatograms offer still another comparison. Sorbent FAST-ACT with high yield decomposed agent VX quite in terms of the content of propagation materials of a producer. However, the decontamination glove which is filled with the same sorbent, even after 24 hours contained a large amount of the agent VX. This means that the contaminant remains in the surface layer of a fabric through which it does not reach the sorbent. This fact might be one of the causes of a low decontamination effectiveness of the means [6].

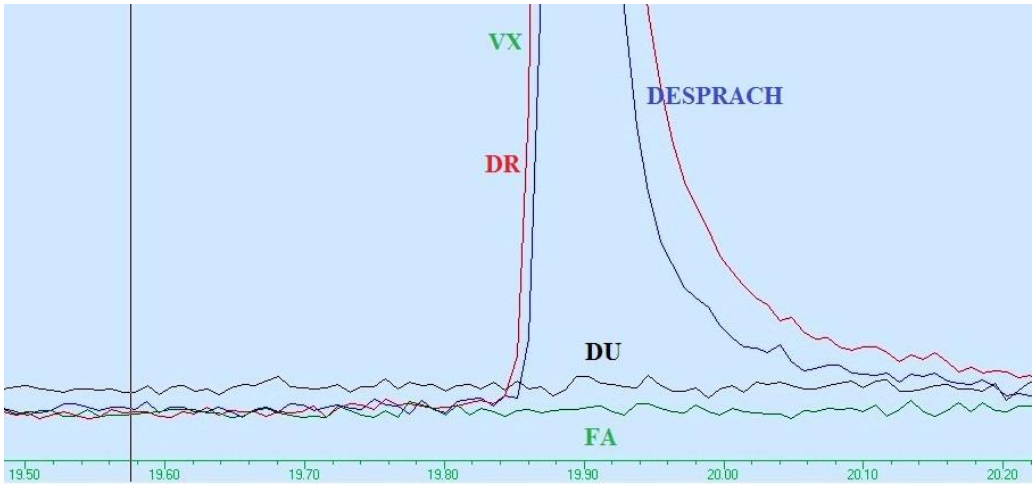

Fig. 2
Chromatogram of waste after the decontamination of VX agent by sorbent DESPRACH, decontamination glove (DR), sorbent FAST-ACT (FA) and a decontamination cloth RSDL (DU) – detail of a chromatogram of Fig. 1

The Waste Generated after the Decontamination of Sulfide Yperite

After the decontamination of sulfide yperite, the waste after the application of sorbent DESPRACH, decontamination glove (see Fig. 3) even wiping with ethanol represents again an increased waste risk. On chromatograms there are significant peaks of yperite at retention time around 13 minutes.

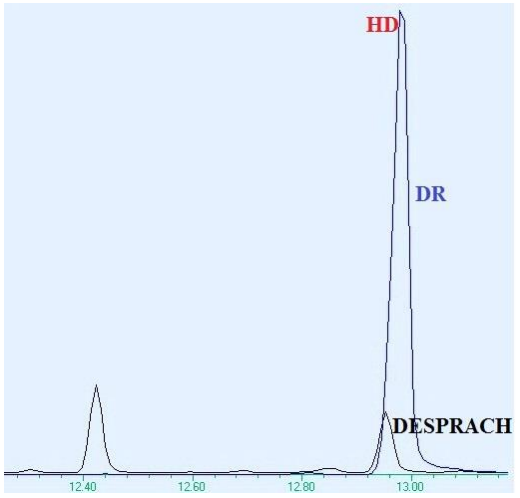

Fig. 3
Chromatogram of the waste after the decontamination of sulfide yperite by sorbent DESPRACH and decontamination glove (DR)

Chromatogram in Fig. 4 shows that both sorbent FAST-ACT (blue chromatogram), and decontamination cloths RSDL or the Czech prototype of a cloth (black chromatogram) decompose yperite with high effectiveness to products declared by producers. In the waste after the application of a cloth we found a slight amount of yperite which represents an insignificant risk. Sorbent FAST-ACT decomposed the contaminant completely. This conclusion and a high content of yperite in the glove again confirmed the discrepancy specified in the evaluation of the waste after the decontamination of VX agent.

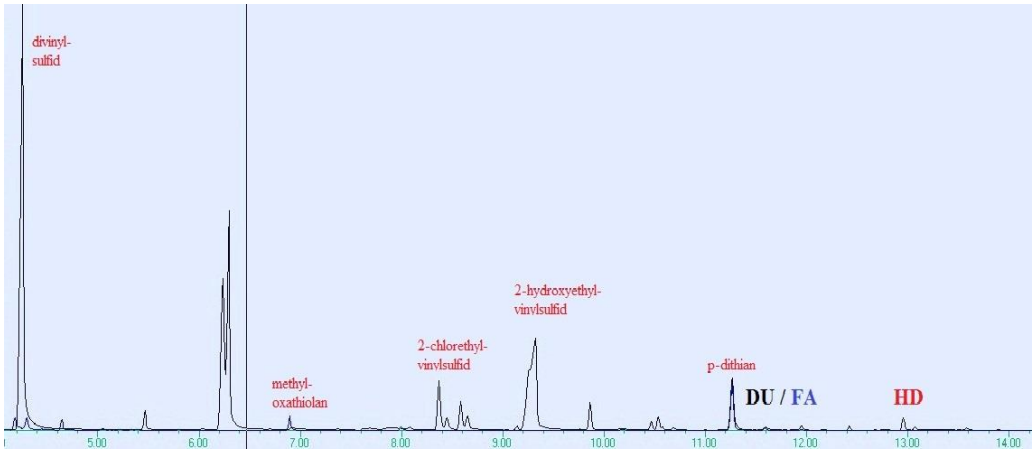

Fig. 4
Chromatogram of the waste after the decontamination of sulfide yperite by sorbent FAST-ACT (FA) and a decontamination cloth RSDL (DU)

The Waste after the Decontamination of O-cresol and Acrylonitrile

Equally as in the case of VX agent and yperite we analyzed the waste after the decontamination of o-cresol and acrylonitrile. Relevant chromatographs are specified in a research report [2].

We discovered that both the decontamination cloths and sorbent FAST-ACT do not decompose these contaminants to non-toxic products. In this case it is the decontamination based on a physical principle and not on a chemical one. The cloth is applied for wiping the surface with the dissolvent and regarding the means FACT-ACT it is a single sorption. However, it is necessary to remind that the cloth is primarily determined for the decontamination of chemical warfare agents.

Partial Conclusions from Waste Risks Testing

During the decontamination of industrial injurants by the application of all tested means and procedures, dangerous waste was produced and the level of this risk is dependent on the toxicity of a contaminant. The conclusion for means based on a physical principle is the same also for the decontamination of chemical warfare agents.

The evaluation of the waste risks after the application of the means of individual decontamination results in a simple question: „**What to do with it?“ Neither the instructions**

nor the methodic materials respond to this question. Merely the instructions for the decontamination cloth say that the waste is disposed according to valid legislation of a state.

It is necessary to admit that especially decontamination means for chemical warfare agents determined first of all for the army do not suppose only a minor local problem but vast contaminated territory where a contaminated cloth or sprinkled sorbent relatively do not represent a risk which has to be addressed. However, regional fire rescue units do not assist in large contaminated areas and during their urgent attendance the following situations might occur:

- a firefighter has on his hand a highly contaminated glove,
- residues after decontamination are highly contaminated cloths or blanks after wiping with alcohol,
- after the application of sorbent on a vertical surface, a gentle, highly contaminated sorbent spreads around this decontaminated surface and falls down not only on the ground which is then contaminated, but it threatens also the persons who might inhale it.

Again, it is necessary to emphasize that no methodology addresses this discrepancy. In order not to transfer contamination from one place to another, but a factual decontamination, the regional fire rescue units would have to be equipped with another means for waste disposal.

Proposal for Waste Disposal after Applying the Procedure Based on Wiping Surfaces with Ethanol

No commercial means are available for the application of the procedure based on wiping with ethanol. This enabled the authors to propose their own procedure of waste disposal [10]. It is based on the gathering of all tampons used for wiping of surfaces in a container and sprinkling with solid sodium hydroxide. The examples of chromatograms in Fig. 5 and 6 show the resulting effect.

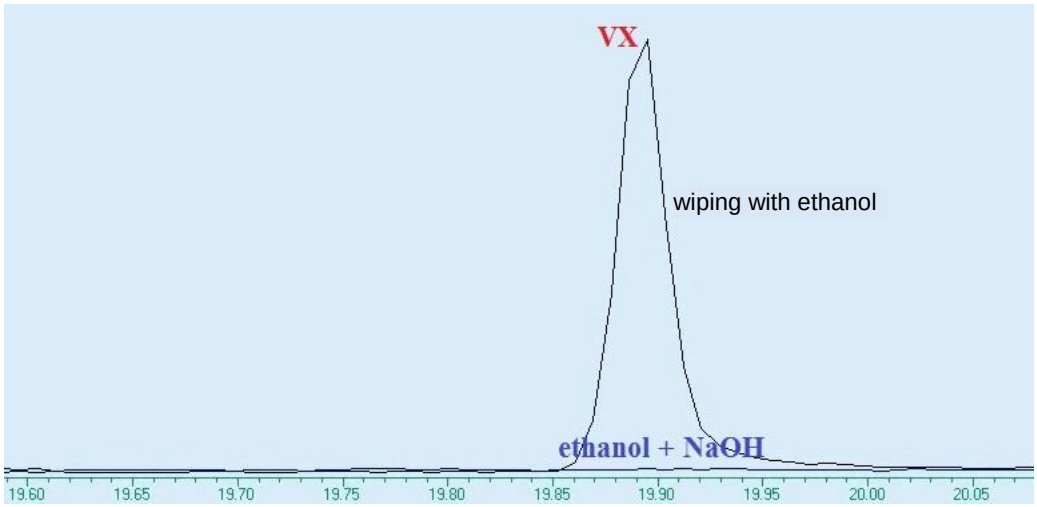

Fig. 5
Chromatogram of waste imminently after decontamination of agent VW by wiping the surface with ethanol ("wiping with ethanol") and after sprinkling by sodium hydroxide and 24 hours exposure ("ethanol + NaOH")

After 24 hours of the application of hydroxide, no contaminants were identified in waste blanks and the waste risk is, this way, significantly reduced. Waste chromatograms after the decontamination of agent VX (Fig. 5) and also sulfide yperite (Fig. 6) show that high concentration of sodium hydroxide in water-alcoholic environment is the environment suitable for their decomposition. Yperite is decomposed into similar products as in case of the application of a decontamination cloth or sorbent FAST-ACT.

Also acrylonitrile is decomposed and in decomposition products non-toxic sodium propionate prevails. In case of o-cresol there is no decomposition process, but it reacts to cresolate sodium which does not threaten, in any case, persons when inhaled.

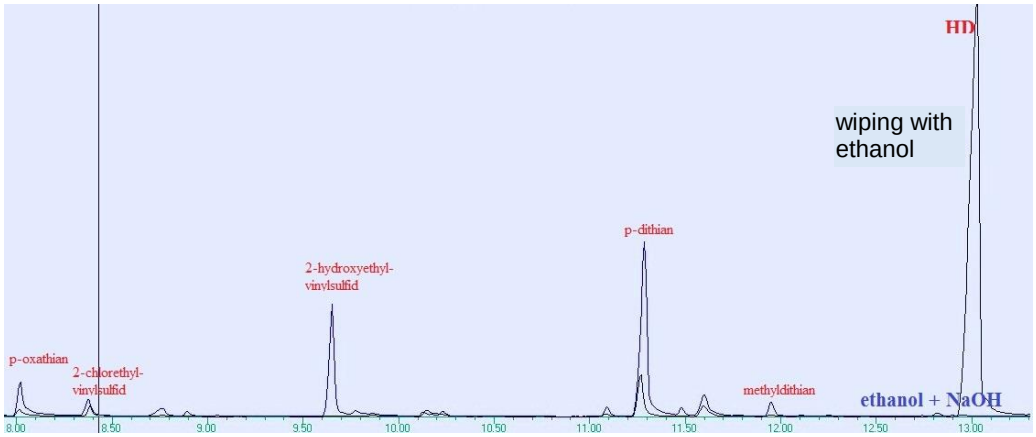

Fig. 6
Chromatogram of waste imminently after decontamination of sulfide yperite by wiping surfaces with ethanol ("wiping with ethanol") and after sprinkling by sodium hydroxide and 24 hours exposure ("ethanol + NaOH")

TOTAL EVALUATION OF TESTED PROCEDURES AND MEANS

Total evaluation of tested procedures and means is in Table 1 which includes also results of previous testing of decontamination effectiveness [6]. For clarity, positive parameters are highlighted in bold letters and negative in italics.

Table 1
Total Evaluation of Tested Procedures and Means

Parameter	***Sorbent DESPRACH***	***Sorbent FAST-ACT***	***Glove FAST-ACT***	***Cloth RSDL***	***Cloth Czech Prototype***	***Applicator of Foam Hvězda***	***Wiping with Ethanol***
Decontamination Effectiveness on Chemical Warfare Agents	**very high**	**slightly lower than Desprach**	*low*	**slightly lower than Desprach**	**slightly lower than Desprach**	**in comparison to Desprach lower on VX, higher on yperit**	**comparable to Desprach**
Decontamination Effectiveness on Selected Industrial Injurants	*lower*	*very low on cresol*	*very low on cresol*	**comparable to Desprach**	**comparable to Desprach**	not tested	**very high**
Possibility to Decontaminate Heavily Accessible Places	**yes**	**yes**	*with difficulty*	**yes**	**yes**	**yes**	**yes**
Possibility to Decontaminate Vertical areas	*with difficulty*	*no*	**yes**	**yes**	**yes**	**yes**	**yes**
Need of Water for Rinsing	**no**	**no**	**no**	*yes*	*yes*	*yes*	**no**
Possibility to Decontaminate under Frost	**yes**	**yes**	**yes**	*yes without rinsing*	*yes without rinsing*	*no*	**yes**
Risk of High Toxicity of Waste after Decontamination of CHWA	*yes*	**no**	*yes*	**no**	**no**	**no**	*yes*
Risk of High Toxicity of Waste after Decontamination of Industrial Injurants	*yes*	*yes*	*yes*	*yes*	*yes*	*yes*	*yes*
Set Procedure for Waste Disposal	*no*	*no*	*no*	*in general*	*no*	*no*	**yes** [a)]
Expiration time, Years	not known	**5**	**5**	*3*	*3*[b)]	*3*[b)]	not set
Decontamination Surface, dm^2	**10**	**50** [c)]	*4*[c)]	*4*[c)]	*4*[c)]	*4*[c)]	-
Repeatability at one Means	**yes**	**yes**	*no*	*no*	*no*	*no*	*no*
Price for 1 Piece, Czech Crowns without VAT	not been produced any longer	*4000,-* [b)]	*555,-*	*750,-*	*700,-* [b)]	not been produced yet	-

Notes to the table:

a) See previous chapter.

b) The estimation of authors based on the comparison with a similar product.

c) Decontamination area is not set by the producer. The value is dependent on initial density of contamination and was estimated on the own experience with the means application.

Specific individual tested means and procedures of individual decontamination can be, based on their study, briefly evaluated as follows:

1. Sorbent **DESPRACH** was chosen for this work as a reference one. It is highly effective on chemical warfare agents, medium effective on other injurants. Manipulation with it is very simple, a problem occurs during decontamination of vertical surfaces when gentle particles of sorbent with a contaminant fall on the ground, particles might whirl due to the airflow which represents a risk of inhalation poisoning. The toxicity of waste can be considered as a decisive disadvantage of the means. Sorbent is applicable also for decontamination of uncovered skin.
2. **Sorbent FAST-ACT** represents a modern means with good decontamination effectiveness and the main advantage in comparison with means DESPRACH is the fact that it decomposes absorbed Chemical Warfare Agents, so in case of these contaminants it is not necessary to solve high toxicity of waste. Its application form, which is a plastic bottle itself with 0.5 kg of sorbent, enables unlike the majority of other means multiple application, but on the other hand, it is possible to apply it only on horizontal surfaces.
3. **Decontamination Glove FAST-ACT** contains the above mentioned sorbent; however, in comparison with the application of sorbent itself it does not have its main positive properties which are satisfactory decontamination effectiveness and decomposition of chemical warfare agents. On the contrary, it enables decontamination of vertical areas and ceilings and therefore it does not have the main disadvantage of the previous means. The tested application form of a glove can hardly ensure an efficient contact with the active surface of a glove along the whole contaminated area. The analysis of waste then proved that the active („absorptive“) fabric of a glove does not transmit sufficiently a contaminant to sorbent a so it remains contaminated on the surface.
4. **Decontamination cloths** – two of them were tested; i.e. type RSDL and the Czech prototype. Both cloths are very similar regarding the effectiveness of decontamination and other parameters therefore the following conclusions are valid for both of them. They are effective decontamination means which were dermatologically tested and are applicable even on uncovered skin. They have properties typical for a modern means of individual decontamination (low weight, small size, simple use, high effectiveness). They decompose a contaminant after wiping the surface contaminated by chemical warfare agents. For other injurants we can apply a physical principle of dissolving in an organic solvent which is sufficiently effective; however, dangerous waste is produced. A crucial disadvantage is the price, especially due to a three-year expiration time.
5. **Applicator of Foam Hvezda** represents according to the authors a perspective means of individual decontamination. It was successfully verified only in the decontamination of chemical warfare agents. Sufficient effectiveness was proved for both contaminants. A negative feature was a considerable damage of the paint of a steel plate after the application. According to the information of investigators the development of this applicator has not been completed yet and a standpoint for its production has not been taken as well. Therefore any evaluation is premature and we have not had enough background information about it.

6. Decontamination procedure based on **wiping with ethanol** in table 1 shows the lowest number of „minuses“. Therefore this procedure was further elaborated up to a specific means and methodical procedure [10]. Main advantages of the procedure in comparison to other tested procedures are the following:
   - in average the most effective procedure on all tested contaminants,
   - the cheapest procedure,
   - the only procedure which addresses hazardous waste disposal,
   - the procedure is applicable for temperatures far below 0 °C,
   - the procedure with high level of flexibility and with many possible variants or embodiment.

This way formulated conclusions are related to results of introduced testing of means of individual protection. In any case they should not cause a sensation that the applicability of known technical means and the development of new ones are unfounded. It is important to realize that the evaluation of tested means was carried out due to the needs of regional units of FRS who have to respond to hazardous materials in average 14 times a day. However, a decisive incentive to the research of new decontamination principles and the development of responding technical solutions is the need of the army in case of specific conditions, i.e. when deployed in combat. Under the conditions when vast territory might be contaminated together with military troops, their equipment and armament, obviously, it makes no sense to deal wit minor waste disposal. Regarding the aspect of high decontamination effectiveness of the procedure of wiping with ethanol it is necessary to remind that whilst the testing of the effectiveness of other means was carried out exactly according to the instructions for the means, the application of ethanol was performed according to our own methodology. This method is based on sucking of contaminant drops and a three-time wiping of the surface always with “pure” ethanol. It is logical that the effectiveness of such procedure must be higher than the effectiveness when the surface is not wiped at all or when it is wiped all the time with the same mixture.

Résumé

The article evaluates tested means of individual decontamination, especially their user properties, waste risks and waste disposal, economic demands and other aspects. The comparison results in the fact that all tested commercial means are characterized by some disadvantage for example high price, short expiration time, need of water for rinsing, high risks of contaminated waste etc.

Comparing the procedures, the procedure based on the wiping with ethanol appears the best. Evidently, it is the cheapest procedure, highly effective on all tested contaminants and is characterized by resolved way of hazardous waste disposal, by the applicability at very low temperatures far below zero and by simplicity of implementation on heavily accessible places and vertical surfaces.

This article was created within the project "Security of citizens – Crisis Management" (VF20112015018).

Literature

[1] CAPOUN, T. and J. KRYKORKOVA. Ensuring of Individual Decontamination of Hazardous Chemicals at FRS CR. Part 1: Importance and Means of Individual decontamination. *The Science for Population Protection*, 2013, Vol. 5, no. 3, p. 5–19.

[2] CAPOUN, T. and J. KRYKORKOVA. *Comparison of Selected Procedures and Means of Individual Decontamination.* [Research Report]. Lazne Bohdanec: MoI – GD FRS CR, Population Protection Institute, 2012. p. 67.
[3] SKALICAN, Z. Decontamination. In: PITSCHMANN, V. et al. *Chemical Weapons and Protection against them.* Prague: MANUS, 2011. p. 135–161. ISBN 978-80-86571-09-6.
[4] CABAL, J. Primary Decontamination of Persons. In: PITSCHMANN, V. et al. *Chemical Weapons and Protection against them.* Prague: MANUS, 2011. p. 162–170. ISBN 978-80-86571-09-6.
[5] CASTULIK, P. and J. SLABOTINSKY. Decontamination of Persons – Myths and Reality. In: *Collection of lectures from 12th Annual International Conference „Population Protection – DEKONTAM 2013".* Ostrava: SPBI, 2013, p. 19–24. ISBN 978-80-7385-122-4.
[6] CAPOUN, T. and J. KRYKORKOVA. Ensuring of Individual Decontamination of Hazardous Chemicals at FRS CR. Part 2: Comparison of Decontamination Effectiveness of Selected Means and Procedures. *The Science for Population Protection*, 2014, Vol. 6, no. 2, p. 93–103.
[7] *Chemical Hazard Containment and Neutralization System*. User Manual. Manhattan: NanoScale Corporation. p. 7.
[8] CAPOUN, T. and J. KRYKORKOVA. *Pilot Tests of Decontamination of CHWA at Low Temperatures.* [Research Report]. Lazne Bohdanec: MoI - GD FRS CR, Population Protection Institute, 2013. p. 49.
[9] *Identification of Substances by Method GC/MS*. 3rd edit. [SOP I03]. Lazne Bohdanec: MoI – GD FRS CR, Population Protection Institute, 2012, p. 22.
[10] CAPOUN, T. and J. KRYKORKOVA. *Project of Kit for Individual Decontamination of Firefighter INDEHA.* [Research Report]. Lazne Bohdanec: MoI – GD FRS CR, Population Protection Institute, 2012, p 22.