DE GRUYTER OPEN
International Conference KNOWLEDGE-BASED ORGANIZATION
Vol. XXIV No 3 2018

EVALUATION OF BREAKTHROUGH TIME OF SELECTED CHEMICAL WARFARE AGENTS THROUGH PROTECTION MATERIALS UNDER STATIC CONDITIONS WITHIN THE INTERLABORATORY METHODS COMPARISON

Pavel OTŘÍSAL*, Iva VOŠAHLÍKOVÁ, Jiří SLABOTINSKÝ**, Markéta WEISHEITELOVÁ**, Vladimír OBŠEL***, Stanislav FLORUS***

*** Nuclear, Biological and Chemical Defence Institute of the University of Defence in Brno, Vyškov, Czech Republic**
**** National Institute for Nuclear, Chemical and Biological Protection, Kamenná, Milín, Czech Republic**
***** DEZA, Brno, Czech Republic**
Pavel.Otrisal@unob.cz

Abstract: *Based on long-term experiences cooperation between the Laboratory of Toxic Compounds at the National Institute for Nuclear, Chemical and Biological Protection and the Nuclear, Chemical and Biological Defence Institute of the University of Defence in Brno an interlaboratory double-sided comparison has been established in recent time. The interlaboratory comparison of methods is one of several quality management tools according to ČSN EN ISO/IEC 17 025:2005. In the Czech Republic a commercial available comparison system for breakthrough time determination of chemical warfare agents through protection material actually does not exist. In fact the methods are somewhat narrowly focused. Several procedures for evaluation of protection materials properties to drops and steams of soman or sulphur mustard under static conditions have been performed. Detection of chemical warfare agents has been realized by using suitable chromogenic indicator. This article summarises evaluation of the realised interlaboratory comparison.*

Keywords: soman, sulphur mustard, 3,3-Dimethylbutan-2-yl methylphosphonofluoridate, 1-Chloro-2-[(2-chloroethyl)sulfanyl]ethane, Chemical Warfare Agent

1. Introduction

Routine analyzes with samples containing Chemical Warfare Agents (CWAs) bring the same demands of a quality of the result as any other safer analytical procedures. On the other hand, working with highly toxic substances is a specific area. It is necessary to not only minimize the used amount of hazardous substances but also to ensure the shortest possible handling time from the point of view of work safety. From a very strict point of view, these approaches go a little against each other. However, considering all the benefits and risks, it is possible to say that performing the comparative test provides information that can benefit the participating laboratories. The study dealt with a comparison of routinely used methodologies for which commercially available proficiency testing programs do not exist, and, moreover, where performance assurance is usually validated "only" by internal control samples. The interlaboratory comparison

DOI: 10.1515/kbo-2018-0153

brings a higher quality of test results because it can help to refine the uncertainties of the set values.

2. Samples Preparation

2.1. Selection of Materials for Testing

These tested materials have been used for the study of resistance against the permeation of sulfur mustard (HD) and soman (GD) in the framework of the interlaboratory test comparison (ITC):

1) butadiene - acrylonitrile + butadiene - styrene rubber (AGRO, Brno, Czech Republic), hereinafter marked as "NBR/SBR",
2) the foil from polyethylene - vinyl acetate which is used for the production of disposable raincoats JP-90 (Fatra, Napajedla, Czech Republic), hereinafter marked as "PEVA",
3) polyethylene sheathing protective foil of the LDPE type (low density polyethylene), further labeled "PE",
4) TP-RUB-001-06 fabric made of polyamide textile with both-sided coating of the polymeric butyl-rubber mixture (Rubena, Hradec Králové, Czech Republic, Náchod factory), hereinafter labeled as "OPCH-05".

Samples from the non-original length supplied by a client have not been neither modified nor treated before use. Samples have been tempered according to the ITC specifications before the own analyses.

2.2. Test chemicals and other chemicals

2-(Fluoromethylphosphoryl)oxy-3,3-dimethylbutane (SOMAN, GD) purity min 95 %, Bis(2-chloroethyl) sulfide (sulfur mustard, HD) purity min 95 %, Congo red color, Tetrachloromethane p.a, chloroamide CNITI-8, 0.5% solution of sodium diethyldithiocarbamate, p.a., ethanol, denaturated, potassium dichromate, p.a., sodium citrate, p.a., benzidine hydrochloride, purified.

2.3 Independence of participating laboratories

The set samples has been tested in the Laboratory of Toxic Compounds at the National Institute for Nuclear, Chemical and Biological (NBC) Protection, public research institution which is accredited for these types of test in accordance with the norm of ČSN EN ISO/IEC 17025:2005 (the contracting authority of the ITC). The NBC Defence Institute of the University of Defence in Brno has been the second participating site. Each laboratory has received a set of samples from the same metric component of the selected materials. A reference set of samples with the same materials has been stored in a sealed envelope at a segregated workplace of the National Institute for Nuclear, Chemical and Biological Protection directly in the Laboratory of the chemical monitoring and protection in Brno for the possibility of occasional experiments´ repetition.

2.4 Defined conditions of samples contamination

The samples have been contaminated with a filter disc (frit) completely wetted in the test chemical. Before placing the filter disc on the surface of the tested material, excess contaminant was drained. Samples have been tempered for minimally 1 hour, to reach the temperature of 30.0 ± 0.5 °C.

3. Samples Preparation

3.1. Accredited methodology MAZL 03/95/ Mikrotest: determination of breakthrough time of protective materials against drops of sulfur mustard under static conditions on acid-base indicator

Saturated sulfur mustard vapors, whose source fritted places with a liquid phase of the test chemical are, permeate through the tested material and react on the ruby side with the indicating paper after penetration. The cellulose paper 0.10-0.12 mm thick is stained with Congo red color which has been preactivated with CNITI-8 chloramide (CNITI-8 solution in chloroform prepared by benz-*o*-toluidine chlorination). The color transition of the impregnated paper from red to blue color is caused by reaction with hydrochloric acid released in the reaction of

permeating sulfur mustard with CNITI-8 (pH reduction in the scope of 5.5-3.0) [1-4]. The permeation time, thus the time between the beginning of exposure and the first observable coloration of the fabric, is referred as the sulfur mustard breakthrough time BT_Y. The experimental set was tempered at the demanded temperature of 30.0 ± 0.5 °C during the whole test.

3.2. Accredited methodology MAZL 36/10 Permeatest 3 (cupral method): determination of protective properties of materials against drops and steams of soman and sulfur mustard on colorimetric indicator

The vapors of the sulfur mustard permeation through the tested material by convection and diffusion form a white precipitate with an aqueous solution of cupral (sodium diethyldithiocarbamate) placed behind the material. The first noticeable turbidity (opalescence) of the indicating solution indicates the permeation of the sulfur mustard [5,6]. At all times, the test is carried out at a defined temperature of 30.0 ± 0.5 ° C.

3.3 Accredited methodology MAZL 36/10 Permeatest 3 (methodology in accordance with Schönemann): determination of protective properties of materials against drops and steams of soman and sulfur mustard on chromogenic indicator

The soman steams permeating through the tested material by convection and diffusion react with the water-alcohol Schönemann´s solution (thus benzidine hydrochloride, sodium perborate, sodium citrate) placed behind the material to form a yellow solution. The color intensity of the solution is compared with the color intensity of the 0.004% potassium dichromate standard solution corresponding to a soman concentration of $5 \cdot 10^{-3}$ g/cm^2. The time of permeation, thus the time between the beginning of exposure and the comparable staining of the detection solution, is referred as the soman breakthrough time BT_{So}. The test was carried out at a defined temperature of 30.0 ± 0.5 ° C.

4. Results

Tables 1 to 3 contain a summary of the results obtained by the measurements in the two independent laboratories mentioned above. Results of the mutual comparison showing the breakthrough time less than 8 hours were plotted in graphs (Figures 1-3). Each value was given introduced with a two-sided error line that corresponds to the confidence interval $L_{1,2}$ at the 95% responsibility level that was obtained by applying the Student's distribution $t_{1\text{-}P,N}$ to the formula (1) [7]:

$$L_{1,2} = \pm t_{1-P,N} \cdot \frac{s_{x_i}}{\sqrt{N}} \qquad (1)$$

where, s_{xi} = standard deviation of the set x_i and N = the number of measurement.

The thickness of used samples was determined by measuring at five sites of their area - scattering of the obtained values was expressed as a standard deviation.

Table 1 Accredited methodology MAZL 03-95 / Mikrotest - sulfur mustard

Type of tested material	National Institute for NBC Protection			NBC Defence Institute		
	Thickness of foil (mm)	BT_Y (min)	$L_{1,2}$ (min)	Thickness of foil (mm)	BT_Y (min)	$L_{1,2}$ (min)
NBR/SBR	0,496 ± 0,006	41	1,4	0,48 ± 0,01	46	2,8
PEVA	0,108 ± 0,006	24	2,5	0,11 ± 0,00	24	2,9
PE	0,125 ± 0,006	> 24 h*	---	0,13 ± 0,00	> 21 h*	---
OPCH-05	0,310 ± 0,010	255	7,5	0,33 ± 0,00	258	32

***** Measurement has been finished after mentioned time

Table 2 Accredited methodology MAZL 36-10 / Permeatest 3 (cupral method) - sulfur mustard

Type of tested material	National Institute for NBC Protection			NBC Defence Institute		
	Thickness of foil (mm)	BT_Y (min)	$L_{1,2}$ (min)	Thickness of foil (mm)	BT_Y (min)	$L_{1,2}$ (min)
NBR/SBR	0,499 ± 0,016	75	7,5	0,48 ± 0,01	56	1,7
PEVA	0,101 ± 0,010	40	2,5	0,11 ± 0,00	34	2,0
PE	0,129 ± 0,008	> 24 h*	---	0,13 ± 0,00	> 21 h*	---
OPCH-05	0,309 ± 0,008	258	7,5	0,31 ± 0,01	231	15

***** Measurement has been finished after mentioned time

Table 3 Accredited methodology MAZL 36-10 / Permeatest 3 (Schönemann´s method) - soman

Type of tested material	National Institute for NBC Protection			NBC Defence Institute		
	Thickness of foil (mm)	BT_{So} (min)	$L_{1,2}$ (min)	Thickness of foil (mm)	BT_{So} (min)	$L_{1,2}$ (min)
NBR/SBR	0,480 ± 0,008	294	67	0,48 ± 0,01	276	20
PEVA	0,109 ± 0,006	90	3,8	0,11 ± 0,00	115	3,5
PE	0,122 ± 0,008	> 24 h*	---	0,13 ± 0,00	> 21 h*	---
OPCH-05	0,308 ± 0,002	> 24 h*	---	0,31 ± 0,01	503	78

***** Measurement has been finished after mentioned time

The value of BT_Y respectively BT_{So} was calculated as the mean value of five (in the case of the National Institute for NBC Protection), or six (in the case of the NBC Defence Institute) analogously analyzed samples / repeats.

The results show that the confidence interval is not a well-suited tool for approaching measurement uncertainty in this case, because in most cases there is no crossover of confidence intervals between the participating laboratories. It should be taken in mind that within sensory methods the coloring of the operator plays a significant role. This significant fact was not included within the defined confidence intervals. Given that this type of testing is not routinely carried out at the NBCE Defence Institute it was not possible for testing purposes to accurately approximate the uncertainty of measurement for instance by establishing the repeatability of the reference sample analysis in time running.

In general, good agreement can be found between laboratories within BT_Y results determined by the Mikrotest methodology. The second method of BT_Y determination (so-called cupral method) shows a greater dispersion of results between laboratories, which can be done due to the generally worse resolution of the beginning of opalescence.

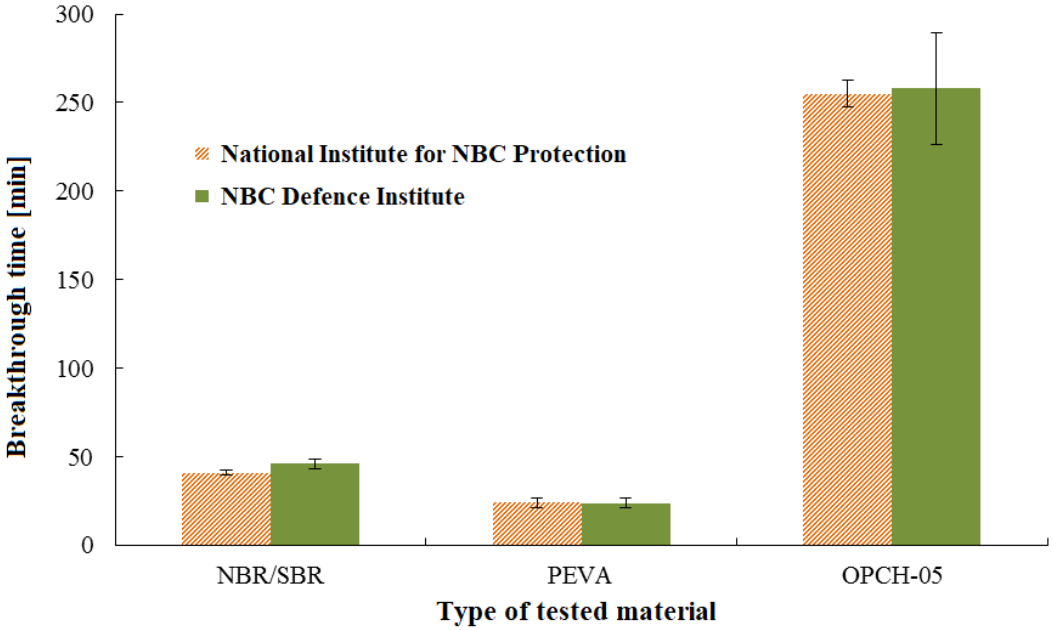

Figure 1 Comparison of breakthrough time selected materials against sulfur mustard - results obtained from two laboratories - the National Institute for NBC Protection and the NBC Defence Institute. Analyzed according to accredited methodology of the National Institute for NBC Protection with internal designation MAZL 03-95 / Mikrotest

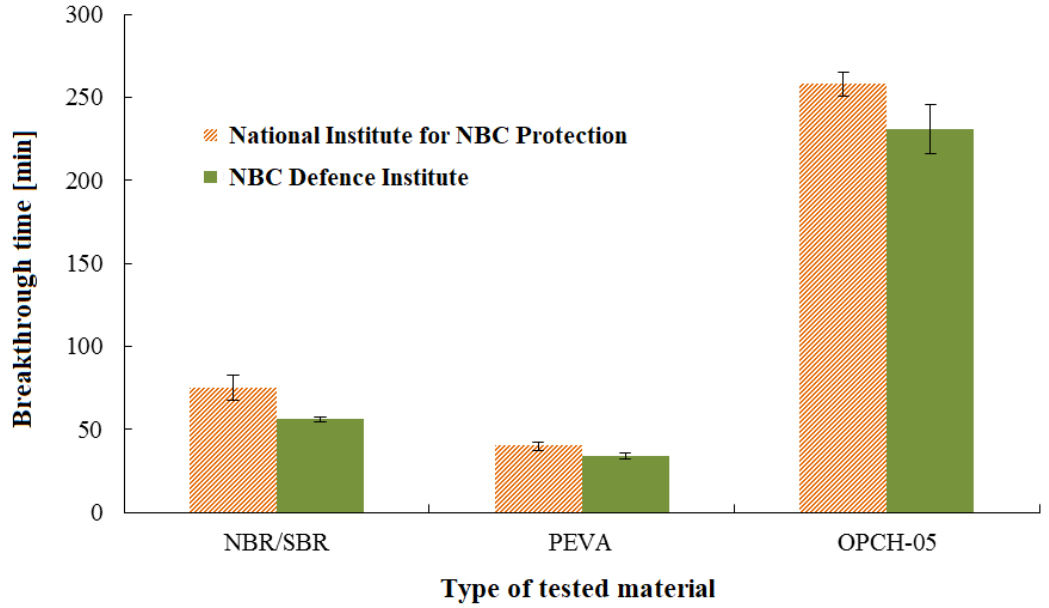

Figure 2 Comparison of breakthrough time of selected materials against sulfur mustard - the results obtained from two laboratories - the National Institute for NBC Protection and the NBC Defence Institute. Analyzed according to accredited methodology of the National Institute for NBC Protection, with an internal designation MAZL 36-10 / Permeatest 3 (Cupral Method)

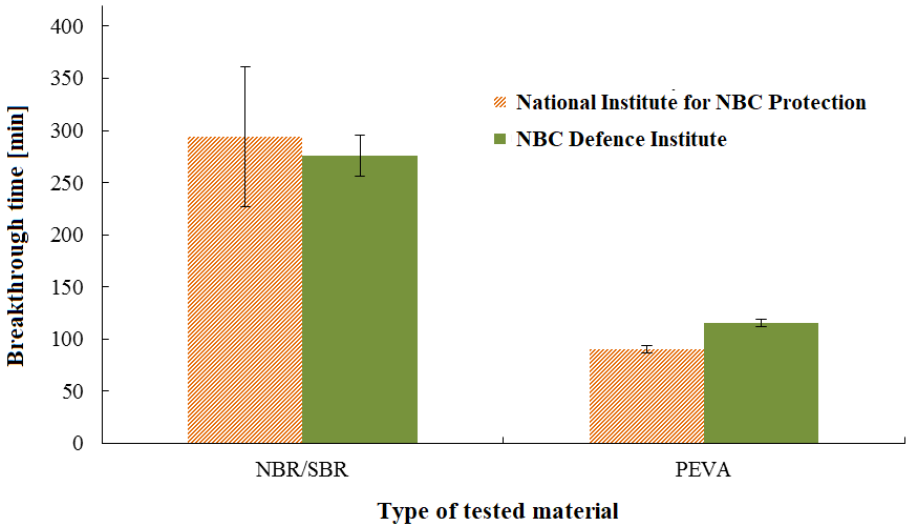

Figure 3 Comparison of breakthrough time of selected materials against soman - the results obtained from two laboratories - the National Institute for NBC Protection and the NBC Defence Institute. Analyzed according to accredited methodology of the National Institute for NBC Protection with an internal designation MAZL 36-10 / Permeatest 3 (method according to Schönemann)

The selected PE material proved to be very resistant both in case of both sulfur mustard and soman contamination. At material thickness ranging from 0.12 to 0.13 mm, resistance was achieved in both laboratories for more than 8 hours. Significant deviations between laboratories were found within OPCH-05 material for soman contamination. In this case, however, the found lower value of the breakthrough time was higher than eight hours. However, the longer duration of a person's stay in protective clothing of a given type in such a high risk environment is relatively unlikely.

5. Conclusions

Interlaboratory comparisons are greatly meaningful in the field of the CWAs analysis. It is especially worthwhile to devote time to such methodologies that are burdened by sensory appreciation. Even today, these methodologies are well-founded. They are, in principle, simple and easy to implement, they consume a minimal amount of toxic substance (test chemical) and they can also serve as methods for pre-engineering instrumental techniques. Due to the narrow specialization, the biggest problem is to find at least one suitable counterpart and participant. Larger light would, of course, be attributed to the participation of at least three laboratories. It would be then possible to use other statistical tools to evaluate the results of the multilateral comparison. Despite these pitfalls, it can be said that the results achieved by the interlaboratory comparison are a good beginning of cooperation between institutions. Finally, the results can help to bring better closeness of the agreement between the result of a measurement and a true value of the measurand within the meaning of accuracy according to GUM [8].

References

[1] SLABOTINSKÝ, Jiří. MAZL 03-95/ Miktorest: D*etermination of breakthrough time of protective materials against drops of sulfur mustard in static conditions on the indicator: Mikrotest.* (in Czech). Kamenná: SÚJCHBO, v.v.i., internal methodology, 1995. 12 p.

[2] VOŠAHLÍKOVÁ, Iva; WEISHEITELOVÁ, Markéta; DROPA, Tomáš. SÚJCHBO Testing Portfolio of Toxicology Laboratories. (in Czech). In sborník mezinárodní konference *„Ochrana obyvatelstva - nebezpečné látky 2015“*. Ostrava: SPBI, VŠB-TUO, 2015, p. 187–190. ISBN 978-80-7385-158-3.

[3] Methodology of VOP-026 Šternberk. Division of VTÚO Brno. MIKROTEST 23 1301 "Set of breakthrough time of protective materials contaminated with drops and gases of sulfur mustard in static conditions (in Czech).

[4] HALÁMEK, Emil, KOBLIHA, Zbyněk, PITSCHMANN, Vladimír. *Analysis of chemical warfare agents* (in Czech). Vyškov: ÚOPZHN UO Brno, 2007. 143 p. ISBN 978-80-7231-258-0.

[5] SLABOTINSKÝ, Jiří. MAZL 36-10/Permeatest 3. *Protection of body surface and breathing organs. Determination of protective properties of materials against drops and steams of soman and sulfur mustard: Permeatest 3*. (in Czech) Kamenná: SÚJCHBO, v.v.i., internal methodology, 2010. 10 p.

[6] FLORUS, Stanislav; OTŘÍSAL, Pavel. Selected Methods of the Study of chemical resistance of isolative protective folios for Chemical Warfare Agents. (in Czech). Chem. Listy *108*, 838-842 (2014).

[7] VYCHODIL, Vilém. *Spot intervals and confidence intervals*. (in Czech). 2011. Probability and statistics. Available from: <http://vychodil.inf.upol.cz/kmi/pras/pr10.pdf>. Made in the framework of the 2963/2011 FRKŠ project

[8] Joint Committee for Guides in Metrology *Evaluation of measurement data — Guide to the expression of uncertainty in measurement*, 1st ed. [online]; JCGM, 2008. (accessed Dec 21, 2017)