



The Qcm Method as a Brand New Method for Testing of Barrier Materials Protective Properties

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Introduction

In current time a lot of technologies effects research activities not only in civilian life but also in military ones. Units and soldiers deployment in operation is closely limited by quality of Individual Protective equipment. The Czech Armed Forces (CAF) Chemical Corps (CCs) specialists are equipped with the special isolative protective garment marked as OPCH-05 which provides an excellent protection against Chemical Warfare Agents (CWAs). Nonetheless, the operational environment has changed in recent time. The global conflict characterized by massive CWAs employment is not considered at this time. Nowadays, the local conflicts connected with terrorists activities conducted in areas without a developed industrial infrastructure. Within these conflicts some Toxic Industrial Chemicals (TICs) can be released and each commander has to provide the best protection to his specialists. In current time it is known that OPCH-05 does not protect CAF CCs properly against the affect of some TICs and it is to be improved. What do scientific workers have to do for improvement of CAF CCs protection?

Middle Paragraphs

As mentioned in the introduction the protective properties of barrier materials have been tested in relation to CWAs in recent time. However, the security threats have changed nowadays and it is obvious that CAF CCs have to be protected against the effect of TICs which is a quite brand new topic for a scientific community. Testing of protective suits is done in the CAF in a stage of their development thus at the time before their establishment into the armament. The protective material used for construction of OPCH-05 was tested in nineties. It is very important to stress that this material is quite the same as used for construction of isolative protective garment marked as OPCH-70. The number refers to the year when the protective garment was established into the armament. Thus, in the case of OPCH-05 it was in 2005. In nineties practically the sole method of MIKROTEST was designated for testing of isolative protective materials in the CAF and its ancestor. In accordance to this method which results from the Military Technical Institute in Brno's [1] methodology a two-stage chemical reaction between sulfur mustard and indication treatment agents is employed. Hygroscopic cellulose

paper colored by the Kongo red color (pH-indicator) is used as a sulfur mustard indicator within this methodology. The paper is activated after its exsiccation with CNITI-8 chloramide [*N*-chlor-*N*-(2-tolyl) benzamide]. An indication principle lies on CNITI-8 chloramide reaction with sulfur mustard. During the reaction hydrogen chloride is released and it changes the alkali form of the acid basic indicator to acid. It is done with a change of the Kongo red color which alternates from red color into the blue one by the way of the azo-hydrazone tautomerism [2]. Indication paper is in a direct contact with a measured isolative folio. The blue-change reveals in a place of CWA (sulfur mustard) penetration. A moment of a threshold amount of the sulfur mustard (0.005 mg.cm^{-2}) penetration is signalized with the first visible blue spot which has an average of 1 mm. Testing is very simple and there is quite no need to use complicated devices. Because the testing is done with real CWA reached results are representative and inform about real tested materials protective properties in face of CWA. During this measurement is necessary to catch the first moment of tested chemical compound penetration on an under-side of tested material which is a basic disadvantage [3-5].

The big advance of the brand new method of PIEZOTEST can be understood in more ways. Firstly, it is possible to study a bigger range of toxic compounds. It means there is a chance to study not only CWAs whose typical representative the sulfur mustard is but also TICs in a liquid phase. Secondly, there is an occasion to study permeation of both CWAs and TICs in more conformity way. While studying of permeation concerning CWAs takes a lot of time during that the observer has to be in the highest condition and keep the attention for long period of time so in the case of TICs' permeation there is no necessity to do it. The main reason is that the method of PIEZOTEST is fully automated and it does not demand the observer's presence within measurement running. A QCM detector is the most important part of a PIEZOTEST device. It is a piezoelectric device, which has a sensor made from quartz. This one works as a quartz crystal microbalance, so called QCM detector. A thin polymer layer is coated on the detector. In this layer study both CWAs and TICs permeated through researched polymer into an area of the QCM detector material are caught. The detector is able to measure weight changes very sensitively namely with nanogram exactness. The weight additions of pollutants in a detector polymer layer reveals piezoelectric crystal working frequency grow which is evaluated as an objective quantity. Thirdly, there is possibility to assess gained data in both simple and sophisticated way. The simple way how to evaluate data is to construct a curve which shows the dependency of QCM detector working frequency change on time. It can be performed quite simply in MS Excel. In this way of evaluation there is no information about permeated concentration of the test chemical. Nonetheless, for quick evaluation of researched barrier material properties in relation to a particular test chemical it is enough. For instance, it can be used in military operations. A commander must decide very quickly about the time how long soldiers can operate in a contaminated area to prevent them against their dermal contamination. The more sophisticated way for barrier material

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protective properties evaluation is to employ especially designed software which enhances possibilities of MS Excel. After recounting of QCM detector working frequency on particular concentration enables to construct dependence of that concentration on time. After that it is possible to read the value of breakthrough time for particular test chemical compound. Because of the PIEZOTEST method is a brand new method no final version of the software does actually exist in the Czech Republic. However, the permeation calculator of PKRV 10 [6] has been tested in recent time in cooperation between the NBC Defence Institute of University of Defence and Military Technical Institute of Protection in Brno. Permeation calculator is designated for application-programme equipment programming in a development environment of MATHLAB in version of R2010b. It serves for calculation of permeation and relevant values for example the values of coefficient of diffusion, breakthrough time and so forth. Calculated values are pictured in graphs. In the same way the values of coefficient of diffusion and breakthrough time are pictured, too. Results are archived in a record for each test chemical. These records can be used for other data analyses. The biggest advantage is a chance to evaluate data in accordance to the norm of ČSN EN ISO 6529 [7]. This software enables to determine these values concerning close-loop detection permeation system:

- Normalized breakthrough detection time within normalization permeation mass of $0.25 \mu\text{g}\cdot\text{cm}^{-2}$;
- Normalized breakthrough detection time within normalization permeation mass of $2.5 \mu\text{g}\cdot\text{cm}^{-2}$;
- So called lag-time (tl) [min]. This one has been found after launching of a "brush" tool in the environment of MATHLAB software;
- Diffusion coefficient (D) [$\text{cm}^2\cdot\text{s}^{-1}$]. From the value of tl it is possible to count the value of D which characterizes a rate of test chemical permeation through researched barrier material. However, values of D have real relevance only within measurement in open-loop, thus in dynamic conditions. In this conditions the concentration declivity between contaminated and opposite site stays constant and output concentration on aired site is close to zero.

In order to answer a question mentioned above there are some tasks to do:

- To test TICs in defined logical lines to make some connection among them. This way of study enables professionals to estimate the effects of particular TIC on a concrete protective barrier material;
- To evaluate gained data in both ways. It means for military (operation) and civilian purposes;
- To establish method of PIEZOTEST into both field and stationary laboratories;
- To organize courses for CAF CCs specialist to manage this method in military operations. This method can be also used within Fire and Rescue Brigades that uses similar individual protective equipment of an isolative type;
- To study special characteristics which enhances the measured results? Very important is to deal with transportation value

such as D and its relationship to the permeation rate;

- to elaborate possibilities how to enhance protective characteristics of current isolative protective folios used in CAF CCs' individual protection ;
- To think of some consequences which can be understand as a challenge in a branch of individual and collective equipment. For instance, this method can be used for study decontamination mixtures influences on changes of protective characteristics of isolative materials;
- To compare gained results from permeation cells based on both open and close loop. It enables to exclude some discussions concerning conditions of special isolative protective garment employment in operations;
- To compare results produced from other research workplaces and universities to make a platform for discussing experiences;
- To enhance software for evaluation possibilities. Results have to be unambiguous;
- To elaborate processes to establish the method in both field and stationary laboratory. After revision of these procedures to offer them into a practical life;
- To confirm the method based on the users point of view and their necessity to work with individual protective equipment in a protection position.

Closing Paragraph

The employment of PIEZOTEST method seems to be a very effective way how to provide information to operational commanders related to barrier materials quality in current time. Furthermore, it is the way how to assess barrier protective materials for civilian purposes, thus in favour of Integrated Rescue System especially for Fire and Rescue Brigades. The employment of this method to the practice life is a challenge how to improve barrier materials used in a branch of individual protection and how to grow trust in them in operations. Information concerning the fact that isolative barrier materials still protects either entirely or only partly provide informational support to commanders for realization of high-quality decisions belonged into the area of either protection against WMD or Chemical Support. On the other hand the information can be useful for a potential purchaser who hesitates within decision process and make his decision simpler.

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