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ORIGINAL ARTICLES

New approaches regarding the protection forces' health against the effects of some toxic substances

Pavel Otrisal[1], Camelia Diaconu[2], Ovidiu Bratu[3], Florentina Ionita Radu[3], Zdenek Melicharik[4], Simona G. Bungau[5]

Abstract: *In the past, finding out the chemical resistance of the barrier materials designated for the production of individual protective equipment ofthe protection forces (policemen, firefighters, soldiers) was based on the need to respond to protection against weapons of mass destruction. Simple chemical methods based on indicating the colorimetric reactions were used. It was necessary to switch to more universal methods due to a change in the security of the environment and the need to focus on toxic industrial materials. The universality is due to using sensitive QCM sensors equipped with a special detection layer and some special carbon electrodes. The paper deals with new methods that are used to determine the chemical resistance of the barrier materials against the permeation of toxic substances, primarily in field conditions. However, they can also be used in stationary chemical laboratory conditions.*

Keywords: *Permeation, barrier material, PIEZOTEST, KONDUKTOTEST, SORPTEST*

INTRODUCTION

Public health is and must be a major interest for the policies and legislation of a country. Maintaining and improving it must be done by implementing appropriate measures and programs, by educating the population and by raising the standard of living. A particular sector within this field of health is represented by the health insurance of the protection forces (police, firefighters, soldiers). In addition to psychological training, physical training, proper nutrition, etc., they must be provided with the optimal equipment to cope with specific interventions. Exposure to various harmful factors (fire, extreme heat, chemicals, pollutants of all kinds, etc.) must take place in the optimum parameters, ensuring the best performing materials, with maximum level of protection [1]. Direct contact with these substances (drugs, chemicals, flammable substances, poisons, narcotics, various medical and pharmaceutical waste) [2-4] which can usually be found in nature and especially in cases of emergency (fire, war, explosions) can often be lethal, through harmful compounds that are released or which, in direct contact with the skin can cause severe burns, major infections, dizziness, fainting, headache, choking, serious pathologies as cancer [5, 6] etc., and finally – death.

The interest to produce protective materials impervious to possible contamination agents has increased in recent years. The political decision makers, as well as the economic agents and the manufacturing companies (that are producing harmful substances, pollutants, as well as those who's

[1] Nuclear, Biolological and Chemical Defence Institute, University of Defence in Brno, Brno, Czech Republic
[2] University of Medicine and Pharmacy "Carol Davila", Bucharest, Romania
[3] University Emergency Central Military Hospital, Bucharest, Romania
[4] Faculty of Physical Culture, Palacký University Olomouc, Olomouc, Czech Republic
[5] Faculty of Medicine and Pharmacy, University of Oradea, Oradea, Romania

Corresponding author: Simona Bungau
simonabungau@gmail.com

activity field involve obtaining the performant barrier materials) concentrate their activity more and more intensely on this aspect of the development of the protective equipment with high quality, reduced cost, with high demand on the market and which generate waste as little as possible following the production process [7-14].

In the last decade, there has been a shift from relatively simple chemical colorimetric methods for testing the resistance of the barrier materials against the permeation of toxic substances to sophisticated methods based on a principle of sensor technologies [15-21]. This change was called by a gradual re-evaluation of the security threats experienced by military professionals in military operations [22, 23]. Representatives of the North Atlantic Treaty Organization declared that high use of weapons of mass destruction is currently unlikely [24]. Industrial chemicals are now considered to be a significantly more important security threat because their leakage can cause many losses and can cause contamination of large areas of interest [25, 26]. New methods that enable the testing of the chemical resistance of the barrier materials against the permeation of toxic substances find their practical application also in testing of already established final products and also of the barrier materials that may find their use in the future [27, 28]. New methods also allow very fast evaluation of the permeation data found and meet all requirements set by military and European standards [29]. The concept of research, development, and production of permeation devices using sensor technologies has been designed to meet the requirements for their use in field conditions and to enable obtaining permeation data with minimal attendance and service [30-32].

All these aspects have led to a gradual decrease in the efficiency of work with colorimetric methods, applicable only for determining the chemical resistance of toxic substances (used in wars) under simulated laboratory conditions. These methods did not allow a detailed analysis at the level of the North Atlantic Treaty Organization nor at the European Union level.

PIEZOTEST method

The PIEZOTEST method uses a QCM (Quartz Crystal Microbalance) based piezoelectric sensor to detect permeated toxic substances. These sensors, which find their application in many technical and industrial applications, have been modified to detect the permeation of the toxic substances through the barrier materials by applying the appropriate detection layer to guarantee the functionality of this sensor as a gravimetric detection device. The 1 Hz sensor's response is reported to correspond to the detection of 1 ng of a toxic substance. This sensitivity is quite enough for operating the measuring device in both field and laboratory conditions. Application and software equipment, which is an integral part of the measuring equipment, allows on-line monitoring of a wide range of standardized parameters. The most important data is the breakthrough time (or also the resistance time) when the permeation mass's (cumulative amount) value is reached for a particular (subtracted) value based on the permeation mass (cumulative mass) versus time graph. However, it can also be specified as the normalized breakthrough time, but only if it relates to the normalized permeation weight (cumulated amount) specified by the relevant standard. For fast data evaluation without the need for application and software equipment, it is possible to use the value of protection time (chemical resistance time) expressed as lag-time, to which the value of diffusion coefficient is automatically recalculated. The time to reach the maximum permeated concentration, which is sometimes referred to as the time of half diffusion flow, is also significant for the purposes of assessing the capture efficiency of the test chemicals through barrier materials. The permeation calculator automatically recalculates the value of the respective diffusion coefficient to this value, which creates a space for comparing the penetration rate of the test chemical through the tested barrier material. The time to reach the maximum permeation rate (when the lag-time is reached) and the maximum reached permeation rate (when the steady state permeation rate is reached) is very important for the evaluation of the breathable barrier materials is very significant. Results of the calibration measurements showed that it is possible to achieve high-quality dependencies of the QCM sensor working frequency increase, thus the concentration of test chemical over time, even though this method was not primarily intended as analytical.

KONDUKTOTEST method

The KONDUKTOTEST method is based on the basic analytical method working on electrochemistry, thus dissociation of ions. It introduces practical knowledge of conductometry into the implementation testing practice and adapts them to the conditions for determining the chemical resistance of barrier materials against the permeation of toxic substances. A significant benefit of the used measuring device is the replacement of very expensive platinum electrodes with glass electrodes. These electrodes are characterized by a very good sensitivity and minimal maintenance and operation requirements. Their further advantage is that they do not experience problems with memory effect, which is an important and limiting factor for the electroanalytical methods. The elimination of this effect is based on the actual needs of measurement when working with very dilute solutions. In practice this means that a very low concentration of dissociated ions is sufficient to form a permeation curve, which serves as a basis for the reading of standard values. This concentration is so low that it does not produce the memory effect of the used carbon electrodes even after their repeated use. The KONDUKTOTEST method uses the dependence of electrical conductivity increaseover time to generate the resulting permeation data and evaluate the effectiveness of barrier materials to withstand to a direct contact with toxic substances. The other standard values are the same as in the previous case. The results of the calibration measurements confirmed the theoretical considerations associated with classical conductometry, which in practice means that high quality results have been achieved.

SORPTEST method

The SOPRTEST method suitably complements the abilities of the above two methods. Its primary use can be seen to determine the chemical resistance of barrier materials under dynamic conditions. Due to the combination of the conductometric measurement and the measurement based on the use of QCM sensors, a unique device has been constructed. It enables the combination of methods and used barrier materials. The permeation cells can be adapted to the particular type of measurement and the test material. In addition to breathable and insulating barrier materials, the sorption properties of the bulk sorbent layers can also be tested. By partial modification of the measuring system it is also possible to characterize filters of protective masks and thus to study their dynamic and static sorption capacity. The source of the gas phase of the test chemical is a test tube fitted with a Peltier´s cooler (condenser). The device enables continuous regulation of air flow during its use within calibration, actual measurement and desorption of QCM sensor. Before starting and during the measurement, it is possible to adjust the temperature, which ensures the transfer of the test chemical into the gas phase and the temperature of the Peltier´s cooler. Permeation measuring cells are tempered separately. A biological incubator has proved to be a suitable device. The SORPTEST measurement device allows the generation of the same standardized permeation data. This approach respects the principle of comparability of the observed permeation data across the older used measurement methods. Application and software equipment of this device enables creation of an output report from measurements. It includes results of calibration measurements and individual graphs characterizing the course of monitored standard quantities. The report also includes data concerning the chemical test that was used, its basic tabulated characteristics and toxicological data.

CONCLUSIONS

Obtaining permeation data characterizing barrier materials in accordance with European standards enables their unambiguous description not only at the national level but also at the European level.This approach will allow describing the barrier properties not only during their use, but also during their development and quality verification. The combination of methods for the implementation the knowledge of physics, sensor technologies, classical analytical chemistry and toxicology has resulted in the construction of very modern and sophisticated measuring systems that meet the highest demands on the quality of the obtained data while maintaining economic rationality.

Compliance with Ethics Requirements
The authors declare no conflict of interest regarding this article

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