PIEZOTEST DEVICE – SUITABLE TOOL FOR CHEMICAL RESISTANCE TESTING OF PROTECTIVE SUITS IN BOTH STATIONARY AND MOBILE LABORATORY CONDITIONS

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Abstract

Permanently more serious threats of TICs employment as a potential terrorist tool, their leakage in case of an industrial incident or the need of the liquidation of illegal dumping places of chemical waste call for skilled knowledge about body surface protective suits and their protective properties.These are mostly expressed by the value of the breakthrough time (BT).BT is measured in accordance with the valid both civilian and military norms usually in a process of their establishment into the CAF armament.In these norms, chemical substances on which protective suits have to be tested are set.A number of ordered substances are only a fraction of TICs which CAF Chemical Corps specialists can meet in operations. BT measurements are generally both due to technology and time consuming very difficult. That is why they are performed in stationary laboratories. The measurements of material resistance in either stationary or field conditions would be possible with a measurement set which uses a QCM detector with a polymer layer as a sensitive unit. This device is not difficult to operate with the accessories of mobile laboratories. It is capable to provide essential information concerning protective construction properties of a suit with the amount of either TICs or mixtures of unknown compounds.

Key words

Breaktrough time, personal protection, chemical protection suit, Quartz Crystal Microbalance, chemical warfare agents, toxic industrial substances, detector, QCM detector with a polymer layer.

INTRODUCTION

The quality of personal protection might be apprehended from two viewpoints. First it means the implementation of protective means into the military armament that are supposed to protect against the range of chemical (toxic) substances and the establishment of information support about real protective properties of construction materials that are used for the production of these means which are to be resistant to above mentioned chemical substances. In case that the

values of the resistant time for a specific chemical substance are not available, we can accept a certain risk consisting in the fact that by virtue of the knowledge of chemical resistance of construction materials for a discovered substance, the approximate protective properties will be deduced for a similar substance. In case of the unknown toxic substances or their mixtures, whatever manipulation with them or the exposure in a contaminated environment is highly dangerous. In this case it is necessary to take indispensable organization and technical measures to decrease the potential impact of these substances effects on persons. One of these measures should be the discovery of a contaminant type and consequent deduction of the resistance of construction materials or the measuring of protective properties of materials for the unknown substances through simple and reliable devices.

1 TESTING OF THE RESISTANCE OF CONSTRUCTION MATERIALS USED FOR THE PRODUCTION OF PERSONAL PROTECTIVE SUITS

Testing of the resistance of construction materials for toxic substances is a very time -consuming process and we can say that endless. It is obvious that the army equipment is subjected to testing for chemical warfare agents (CWA). The testing for industrial chemicals (IC) is carried out according to the introduced norm CSN EN ISO 6529 (83 2732) [1], where recommended liquid chemicals either of an organic or inorganic character are specified. However, the results of testing for practical purposes and the support of a decision making process of a chemical unit commander are insufficient, regardless the reality, that more detailed prediction of the protective suit resistance cannot be carried out in case that there is the necessity to work with a substance which do not respond at all to a chemical structure of tested substances stated in the norm. In an ideal case it would be desirable if an expert chief or a commander of a chemical unit obtained the list of the resistance of the types of suits used for a wide range or chemicals, and the dependence of a resistant time on the insulation of a protective folio on chemical structure of the fabric was defined. This relation is very complex since the insulation protective folio of the suits is not generally chemically homogenous, it means the structure of separate layers (bearing, barrier). Moreover the process of permeation of chemicals through the material could be considerably unpredictable. It is obvious that the provision of all necessary information is the matter of the service which could be provided by experimental or developing organization.

In the Army of the Czech Republic the testing of protective suits is carried out during their development, therefore before introducing the garments into the armament. In the past the resistance measurement was exclusively carried out for chemical warfare agents. At present the garments must be also tested for chemicals listed in the Czech state norm for a relevant type of a garment. Sulfur mustard is typical for testing for the resistance of construction materials of protective suits. The measurement is based on the methodology of Military Technical Department of Protection in Brno and it uses a two-level chemical reaction between sulfur

mustard and indication surfactants. Hygroscopic cellulose paper colored by a Congo red as a pH-indicator is used as an mustard intersection indicator. After the dehydration, the activated N-chlorine-N-(2-totyl) benzamide, marked as chloramide CNITI-8 with sulfur mustard during the release of hydrogen chloride which transforms the alkalic form of acido-bazic indicator into acid. Here then the red form of Congo red is transformed into blue through azohydrazon tautomery. Indication paper is in a direct contact with measured insulation folio and the blue color appears in the spot of the sulfur mustard intersection. The moment of the intersection of a threshold amount of used chemical warfare agent (0,005 $mg.cm^{-2}$) is signalized by first distinct blue stain, the diameter approx. 1 mm. Testing is very simple and not demanding for the devices. Since the testing is carried out with a real chemical warfare agent, the results achieved are representative and respond to real protective properties of tested materials against these substances. The main disadvantage of a mentioned method is the fact that during the whole course of measurement the sample must be observed in order to take up the first moment of the intersection of a tested substance on a reverse side of the tested material.

Testing for industrial chemical substances is considerably more complex and its complexity is given first of all by the used equipment for the detection of an experimental chemical substance permeating through the construction material. Highly sensitive detection systems are required in order to record low concentrations of chemicals. The process of the discovery of the resistance of barrier materials is time consuming because due to the abatement of resistance times it is necessary to make a graph of the dependence of the speed of permeation[1] on time. The time necessary for testing is dependent on the resistant time of construction materials, labor consumption, and the requirements for the education level of an attendant will depend on a chosen detection method. Testing of materials is generally necessary to carry out in stationary laboratories. However, this will, in a final result, depend on a chosen method of measurement and a specific device equipment.

For testing of the resistance of construction materials for industrial chemical substances, the workers of VTÚO Brno developed and at the same time experimentally use the device PIEZOTEST [3], whose simplified construction scheme is given in Figure 1. This device was experimentally verified as well and is used by workers of the Department OPZHN of Defense University. It is the piezo-electrical equipment using a QCM (Quartz Crystal Microbalance) detector. On a quartz crystal a thin polymer layer is laid in which a chemical substance, passed through a tested construction material into a work space of QCM detector, is retained. The detector is able to measure very sensitively the mass changes in a polymer layer and it is done with nanogram exactness. The increase of the mass of the harmful agent in this layer is manifested by the increase of work frequency of a piezo-electrical crystal which is recorded by an evaluation device as an objective quantity. After the convergence of the QCM detector frequency on the concentration, it is possible to design the dependence of this concentration on time and then subtract the value of a resistant time of the material for a tested chemical. For rapid evaluation of the resistance of a tested material we can design the dependence of the increase of work frequency of a piezo-electrical crystal on time.

By extending a linear part of the dependence and its intersection on a time axis we can get orientation values of a resistant time, so called Lag Time for a specific chemical substance and construction material (Fig. 2). Lag Time basically determines the beginning of a stable speed of the permeation of a chemical substance through construction material. The slope of a linear part of a curve shows the speed with which the construction material loses its protective properties.

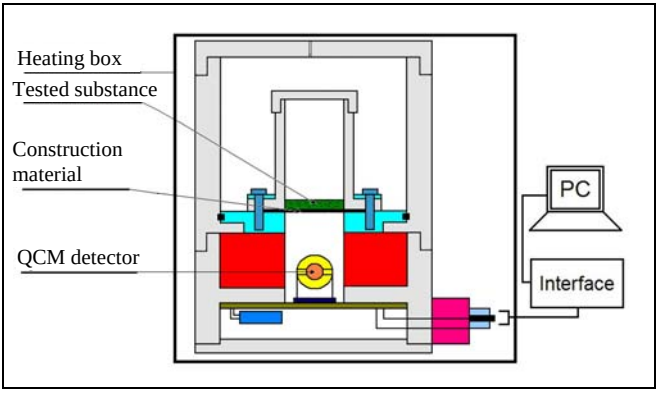

Fig. 1
The scheme of the device PIEZOTEST

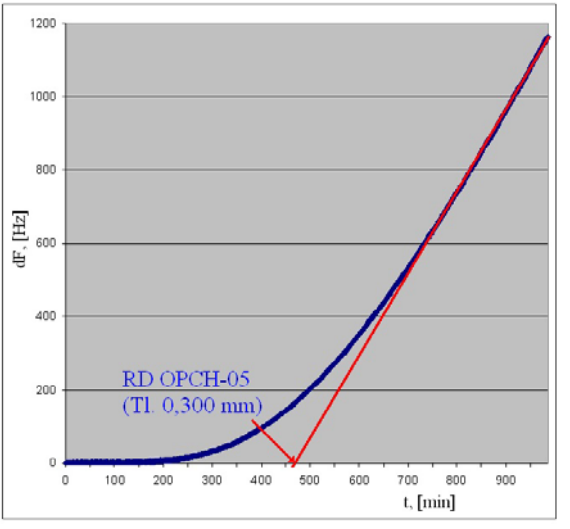

Fig. 2
The scheme of a rapid evaluation of the resistance of construction materials from the dependence of the change of work frequency of a QCM detector on time using Lag Time

Among the advantages of the QCM method of detection we range:

- the possibility to carry out measurements for a wide range of chemicals. The condition is the permeation of substances through tested material;
- the objectivity of measurements. Measured results are not influenced by the threshold of man´s perception, but exactly measurable physical quantity is obtained;
- the measurements can be carried out for theoretical long resistant periods of whatever barrier material which have been already introduced into the armament CHA of ACR and which is also determined for the study of prospectively applicable or new materials designed for the protection of persons against the effects of chemical contamination including so called predatory material or IPM provided within the framework of the support by the host country;
- automatic measurements of pursued values after the preparation and running of the measurement device in the form of a simple software tool connected to a current commercial computer;
- the possibility to evaluate the dynamics of the permeation for a chemical substance and tested material;
- variability of a measurement cell. Using variably constructed parts of a cell for tested material we can carry out e.g. measurements of the resistance of filtration means for protection of the body surface, sorption capacities of sorbents etc. Moreover, modular exchange of the parts of a measurement cell (QCM detector, printed circuit, tiny teflon parts etc.) substantially decreases the costs for its prospective repair;
- relatively low costs of the price of a complete measurement device;
- relatively high resistance against the damage except the QCM detector (the resistance of a detector depends on its construction type);
- simple evaluation of the results of the measurement;
- satisfactory reproductiveness of the measurement;
- the fact, that it is experimentally an easy method which is manageable after a short user´s training;
- the possibility to test construction materials for chemicals in static and dynamic conditions and this way the possibility to study the direct influence of a liquid or vapors (prospectively gases) on explored material. this advantage can be used in the environment of both a stationary and field automobile laboratory;
- the possibility to obtain a large number of results with the application of theoretically unlimited number of measurement cells. At the same time the device can test one type of a barrier material for different chemicals (their number is given only by the number of connected measurement cells) or, on the contrary, various types of materials can be tested for one chemical substance;

- the possibility to provide outputs in an electronic form and their further elaboration by supporting software tools for the convergence of the frequency to a specific amount of a chemical substance that went over the tested material.

The main disadvantages of the QCM detection are:

- quite a long time necessary for the desorption of a tested chemical substance from a polymer layer QCM detector and therefore it is impossible to carry out a one after another series of measurements by the same cells;
- the possibility to damage the QCM detector during the manipulation with a permeation cell (especially after the measurement, therefore during the decomposing of a measurement cell);
- relatively time consuming calibration of the QCM detectors. This calibration is necessary to perform for each detector (each measurement cell) and for each tested chemical substance separately. However, the experiences from the calibration process show that during the calibration of the detectors QCM we can achieve a linear course of calibration curves in a quite large extent of working frequencies.

The simplicity of the QCM detection both technical and operational, the possibility to operate the device in field automobile laboratories and simple evaluation of the resistance of construction materials enable the operation measurement in case of setting in missions. This device is a suitable tool to obtain necessary information on the resistance of materials for unknown substances for operation purposes.

CONCLUSION

The application of the detection method QCM is at present a very effective way how to provide operation commanders with relevant information about the quality of the implemented means of personal protection. The information, whether the actual insulation PPM protect absolutely or just partially, or the declared protective properties for various reasons disappeared or were significantly limited, provide the operation commander with the grounds for the implementation of quality decisions pertaining to the area of protection against WMD or chemical provision of troops.

Résumé

The method of QCM detection seems to be a very useful method for testing the insulation protective suits properties concerning the liquid TICs. This device is very simple for managing and it is relatively cheap. On the other hand it allows to test these materials not only in CAF Chemical Corps but also within Fire Brigades. This measurement tool is tested in conditions of NBC Defence Institute of

University of Defence. The main objective of these tests is to obtain information about the availability or inacceptability of this method for rescue missions abroad.

NOTES:

[1] The velocity of permeation means the amount of a tested chemical substance that permeated through the material of a protective garment on a specific exposition surface per a unit of time.

Literature

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