AiMT Advances in Military Technology
Vol. 7, No. 2, December 2012

Calibration Extension for Permeation Cell of PIEZOTEST Device

S. Florus and P. Otřísal*

NBC Defence Institute, University of Defence, Brno, Czech Republic

The manuscript was received on 9 May 2012 and was accepted after revision for publication on 4 October 2012.

Abstract:

Measurement of permeation resistance of constructive materials against under interest volatile toxic compounds has a huge importance not only from the point of user's view but also from commercial one. It is necessary to distinguish an amount of permeated under interest toxic compound through protective material within both approaches. The PIEZOTEST device is designed for measurement of resistance of square constructive materials used for body surface protection. Commercially delivered device was not able to be calibrated. The aim of this information is to present calibration solution of this device with the help of a calibration extension, available device for dosage. The knowledge of concentration of toxic substances penetrating trough material is needed to calculate to gain information concerning protective properties. Therefore, it is necessary to calibrate a QCM sensor.

Keywords:

Permeation cell, calibration, permeation resistance, breakthrough time (BTT), normalization permeation mass, normalized breakthrough detection time, QCM detector, PIEZOTEST device.

1. Introduction

The measurement of resistance of protective materials is important from the commercial and final user points of view in the branch of individual protection. The final user should know the properties of protective equipment against under interest chemical compounds.

Although, from the logic of things both views should be identical in fact it is possible to find two different approaches to assess the protective properties of

* *Corresponding author: NBC Defence Institute, University of Defence, Sídliště Víta Nejedlého, 682 01 Vyškov, Czech Republic, phone: +420 973 452 335, +420 973 452 330, E-mail: Pavel.Otrisal@unob.cz*

constructive materials. Protective properties of constructive materials are determined by so called breakthrough time (BTT) for the under interest chemicals. Breakthrough time is the time which flows from the first contact of test chemical with a researched material and its detection on the back side of material in predefined quantities or in such quantities which is possible to detect by a particular method. Detection limits for consideration of constructive materials or products have been determined. These limits are set by the values of 0.25 or 2.5 $\mu g/cm^2$ for a close loop in the standard ČSN EN ISO 6529 [1]. These values represent normalization permeation masses which are detected after the use of detection system as normalized breakthrough detection time. Based on measurements of breakthrough detection time the constructive materials, for instance for protective garments production, can be ordered in relation to standard ČSN EN 943-1 (83 2726) [2] into classes of resistance. Afterwards, protective garments can be classified in accordance with resistance against permeation with one of six fixed classes. A principle of a commercial approach is thus ordering garments (protective materials) into some of classes in dependence of time consuming for reaching of permeation of determined amount of tested chemical compounds.

However, a user approach to evaluation of constructive materials cannot come out from permeated amount which is the same for each test chemical, but it should come out from toxicological properties of a particular harmful substance. In practice it would mean that BTT for each chemical or a group of one would come out from maximally allowable amount of the chemical which would penetrate through constructive material on its back side thus, into a direct contact with user's body surface. Breakthrough time defined in this way would introduce the time from beginning of action of particular chemical compound to the time when it would permeate in the amount which would not mean any healthy risk from the toxicological point of view or the risk toxicologically acceptable.

Commercial and user's approaches demand the knowledge of permeated amount of harmful substance through constructive materials.

2. Measurement of Constructive Materials' Permeation Resistance within the Czech Armed Forces

The BTT of constructive materials is measured in a standard way with the help of the MIKROTEST method in the Czech Armed Forces. This method employs sulphur mustard as a test chemical. As an indicator of permeation of sulphur mustard the cellulose paper with neutral leach coloured with Congo red as a pH indicator is used. This indicator is dried and activated with N-chloro-N-(2-tolyl)-benzamide denoted as chloroamide CNITI-8. A principle of an indication is based on chloroamide CNITI-8 reaction with sulphur mustard. During this reaction the acid chloride is released. Acid chloride transfers an alkali form of acidobasic indicator to acid one, thus red colour to blue one in the way of azo-hydrazine tautomery [3, 4]. This method has, however, a lot of lacks. The most consequential one is impossibility to measure breakthrough concentration of test chemical and the possibility to measure only one chemical, thus sulphur mustard.

Regarding the fact that an actual need to measure permeation resistance of constructive materials even for Chemical Warfare Agents and other chemicals from the group of so called Toxic Industrial Chemicals has occurred, the method of PIEZOTEST developed at the Military Technical Institute of Protection in Brno has been established [5, 6]. This method has been verified within army working places and installed in a laboratory practice life [7-11]. This device which used a QCM (Quartz Crystal Microbalance) sensor with a reversible polymeric layer enables to very sensitively find up the mass changes caused with the capture of a test chemical in its polymeric layer which are indicated as the change of working frequency of the QCM sensor connected in an oscillate network of the QCM detector. The moment of permeation of test chemical through constructive material and simultaneously the rate of loss of protective properties of researched material can be determined from the dependence of a change of QCM detector working frequency on time. A single detector is located in a permeation cell whose scheme is introduced in Fig. 1.

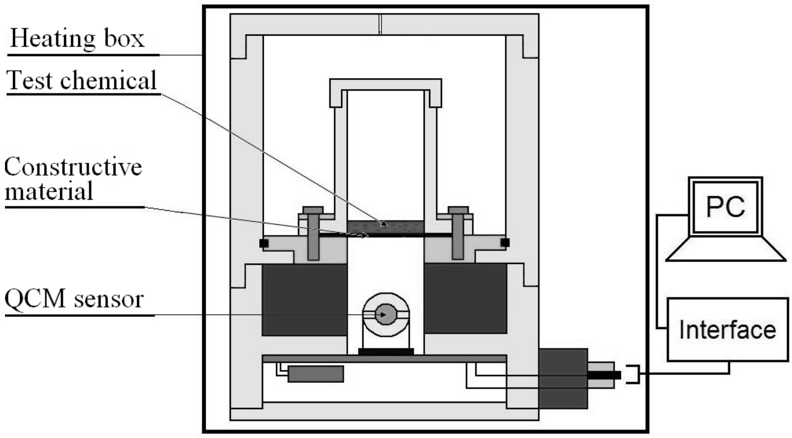

Fig. 1 Permeation cell of the PIEZOTEST device for static conditions

The QCM detector is separated from the test chemical by the researched constructive material within the process of measurement of resistance. The chemical which has passed through researched constructive material and with the help of transport processes permeated to the detector is caught in a polymeric layer located on the detector. It recalls a change of its working frequency. A frequency signal is after that lead through an available interface into a computer where it is recorded, elaborated and evaluated by the help of suitable software.

In the case of this testing set it is not possible to determine permeated amount of test chemical from the change of working frequency of the QCM detector. A solution of this problem is a crucial challenge for both subsequent experimental work and for fulfilment of criteria set in the standard of ČSN EN ISO 6529. In the same way it enables to determine a toxicological impact of dermal exposition on user.

3. The Solution of Permeation Cell Calibration and Transportation of Test Chemical to QCM Detector

The calibration extension was developed in cooperation with Military Technical Institute of Protection in Brno. Regarding a high sensitivity of QCM detector it has been necessary to submit demands which should have been taken into account to guarantee the repeatable calibration of permeation cells. It has been determined that:

- a possibility of charging of small amounts of test chemical in a minimal number of five doses has to exist for a construction of calibration curve;
- charging has to be simple from both the employed testing device and methodology of calibration points of view. This methodology has to be performed in both stationary and field (mobile) laboratory with combat protective aids;
- calibration has to be well reproducible and the scatter of values has to be minimal and comparable with analytical methods regardless of the fact that it is not analytical determination;
- the suitable scatter of chemical compound in a form of gas in a measurement area of QCM detector has to be ensured within calibration of the device thus the transfer from a liquid phase into a gas one;
- the calibration set has to be universal for all permeation cells with no necessity of other changes.

A micro volume syringe of HAMILTON 7001N PST 2 has been chosen as the most suitable after searching of available dosing devices and aids with respecting the specification of permeation cells. This micro volume syringe has ensured enough exactness for calibration purposes. Regarding sensitivity of detectors the micro volume syringe with the overall volume of 1.0 μl with the possibility to dose a volume of 0.001 μl has been selected for calibration.

The selection of the micro volume syringe HAMILTON has a principle influence on construction of the calibration extension. Subsequent demands for its construction have been specified:

- construction of the calibration extension has to enable repeatedly dose the test chemical with respecting exactly determined geometric conditions in order to release the chemical substance into the area of the QCM detector with no QCM detector damage;
- the calibration extension has to be constructed in order to ensure good tightness of the system within test chemical dosage and in order to prevent gases to leak beyond the QCM detector's measurement area;

Within keeping of these demands the calibration extension has been made from Teflon (PTFE), thus from the same material as permeation cells constructed are. The calibration extension has been made in the form of valve which length has been shorter by 0.5 mm in comparison with the length of the micro-volume syringe of HAMILTON. An opening with a diameter of 0.8 mm has been drilled into a centre of a valve in order to insert a needle. An outer diameter has been the same as the inner diameter of a part of permeation cell designated for dosing of chemical compound (Fig. 2). The part of the calibration extension designated for insertion into the permeation cell has been adjusted with turning on the relevant diameter. On this part 2 mm from the end a channel for a seal from chemically resistant material of VITON has been turned. This has been done to totally stuff the area of the QCM detector and to prevent leak of gas of test chemical from the area nearby the QCM detector.

Except dosing test chemicals it has been necessary to solve problems related to their transfer in the form of gas and to prevent possible dropping of those chemicals on the QCM detector at the same time. Placing of a suitable membrane instead of researched barrier material has been the solution. This membrane has enabled to draw a liquid pushed out from the micro volume syringe to increase its surface and to allow effective evaporation. From the whole series the thin polyester fabric without any modification has been chosen. This fabric has good chemical resistance and it has fulfilled set demands on evaporation of test chemicals.

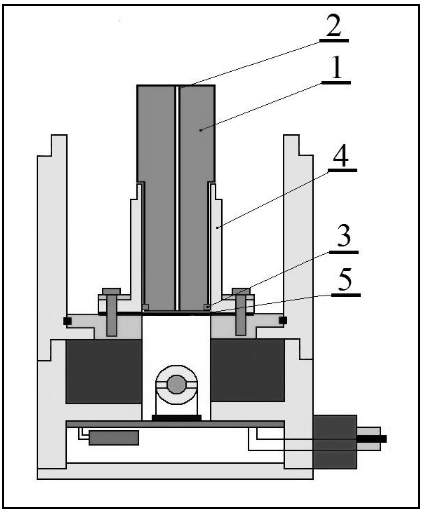

Fig. 2 Permeation cell with inserted calibration extension for calibration in static conditions: 1 – calibration extension, 2 – opening for a needle of the HAMILTON micro volume syringe, 3 – seal, 4 – dosing area of the permeation cell, 5 – permeable fabric

Peculiar calibration has confirmed a reliable construction of the calibration extension. This construction has enabled insertion of HAMILTON micro-volume syringe with no problem. The calibration reduction of extension by 0.5 mm in comparison with the needle has allowed penetration of its tip into the polypropylene fabric. After dosage of the test chemical it has come about its diffusion in the fabric and subsequently to its evaporation into the detector area of the QCM detector. The extension could be used for any permeation cell.

Because of necessity to keep the same temperature conditions within calibration and measurement heating of the permeation cell in calibration duration had to be ensured. A biological incubator has been assessed as the most appropriate for heating of permeation cells within measurement of chemical resistance. On the other hand this incubator has been evaluated as not suitable for calibration from the reason of heat leakage from the heated area. That is why a water thermostat U 15 (VEB MLV Prüfdaräte-Werk/Site Freital, Germany) has been employed as a heat source. An origin lid has been replaced with the lid made from organic glass (PMMA), see Fig. 3.

The lid has been glued from two layers. In a bottom layer the opening has been cut. This one has enabled insertion of calibration extension and determined permeation cell location for calibration. Above it in a place corresponding to its middle the opening has been drilled. This one has enabled to insert the micro volume syringe of HAMILTON. Further opening in the lid has been drilled for sensor for measurement of temperature of PIEZOTEST device in order to document the temperature within performance of calibration. The height of permeation vessel in the thermostat has been fixed with the help of the pad.

Adjustment of PIEZOTEST device for calibration proved to be satisfactory. Calibration device was performed for a variety of chemicals with excellent results particularly for easily and medium volatile organic compounds. In Fig. 4 there are introduced calibration results for cyclohexane, xylene, chloroform, n-octane, 1,6-dichlorohexane and benzylchloride. From Fig. 4 it is clear that calibration curves have almost linear courses. This is documented with high values of reliability in a framework of performed a linear regressive analysis.

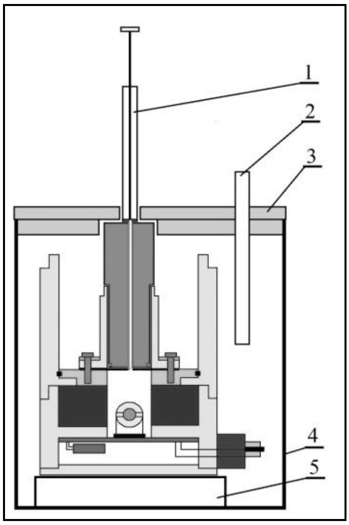

Fig. 3 Heating of a cell within permeation cell's calibration: 1 – micro volume syringe, 2 – sensor for PIEZOTEST device temperature measurement, 3 – lid, 4 – heated vessel of water thermostat, 5 – pad conditioning height of permeation cell regarding to the thermostat lid

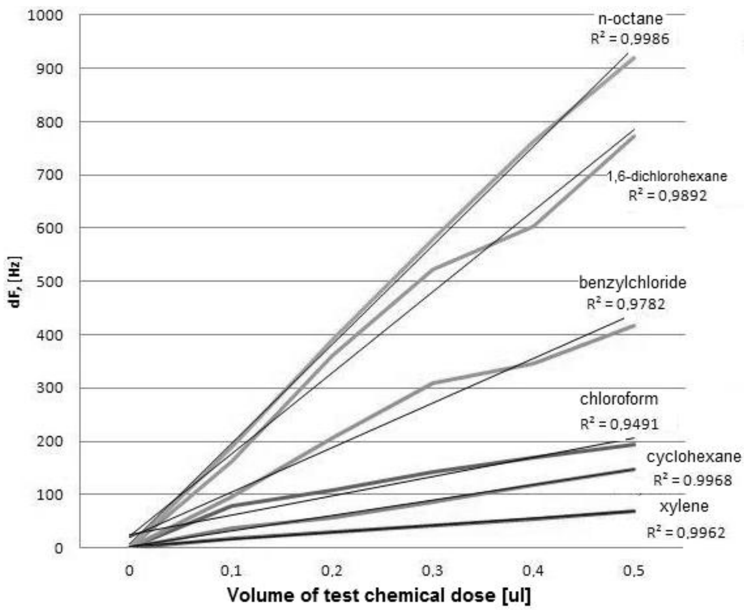

Fig. 4 Calibration curves for selected chemical compounds

4. Conclusion

The calibration extension has extended possibilities of employment of the PIEZOTEST device. Mainly the possibility to read permeated concentrations and their subsequent usage for estimation of toxicological concentration of test chemical enables to more expertly determine time of resistance of individual protective equipment. Based on dependence of the amount of the test chemical permeated through the material it will be possible to determine limit borders of usage of protective equipment in the contaminated area. The possibilities of extension of PIEZOTEST device will quite undoubtedly contribute to development of the individual protection branch.

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Acknowledgement

The work presented in this paper has been supported by the Ministry of Defence of the Czech Republic in institutional development project "Research into new methods and technologies of radiation and chemical protection and the ways of their implementation".