CALIBRATION EXTENDER FOR PERMEATION CELL OF PIEZOTEST DEVICE

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Abstract

The PIEZOTEST device is designed for the measurement of the resistance of square constructive materials used for the body surface protection. Commercially delivered devices are not capable to proceed the calibration. The aim of this information is to present the calibration solution of this device with the help of a calibration extender, available dose device within the calibration of a permeation cell.

Key words

Permeation cell, calibration, resistance, breakthrough time, normalized permeation mass, normalized permeation time, QCM detector, PIEZOTEST device.

INTRODUCTION

In the area of personal protection the measurements of the resistance of constructive materials of protective means are important both for the commercial and end users who should know the properties of used protective means against the chemicals of concern.

The core of a commercial approach is the classification of suits (construction materials) into one of the resistance classes dependent on the time necessary to achieve determined permeation magnitudes. Permeation magnitudes are either the normalized permeation mass during the test in an enclosed loop, or the normalized velocity of permeation during the test in an open loop. Quantitatively both magnitudes are defined by the norm CSN EN ISO 6529 [1]. The time necessary to achieve the determined values of mentioned permeation magnitudes is called the normalized permeation time. According to it, the protective means (construction materials) are classified into one of six resistance classes fully consistent with the norm CSN EN 941-1 (83 2726) [2].

However, the user´s approach to the assessment of construction materials cannot be based on the permeated amount as it is the same for each laboratory substance but it should be based on toxicology properties of a specific harmful

substance. In reality it means that the resistance time for each substance or a group of toxicologically similar substances would come out from the maximally allowable amount of a substance which might permeate through the construction material on its seam side and would get therefore to a direct contact with the user´s body surface. This way defined resistance time represents then the time from the beginning of the effect of a specific chemical substance to the moment when it permeates in the amount which from the toxicological viewpoint does not represent for a user any health risk or the risk toxicologically acceptable.

Both approaches, the commercial and the user´s one require the knowledge about the permeated amount of a harmful substance through construction materials.

1. MEASUREMENTS OF THE CONSTRUCTION MATERIALS RESISTANCE IN THE ARMY OF THE CR.

In the Army of the CR the resistance time of construction materials are standardly measured using the method called MIKROTEST which uses sulphuric yperite as a testing substance. In this method as an indicator of the permeation of sulphuric yperite, the hydroscopic cellulose paper with neutral leach colored by Kongo red as pH indicator is used. After drying it is activated by *N*-chlorine-*N*-(2-tolyl) benzamide, marked as chloramine CNITI-8. The principle of indication is based on the reaction of chloramine CNITI-8 with sulphuric yperite accompanied by the hydrogen chloride release which transfers the alkaline form of the acid-based indicator on the acid one, here then red to blue through the azo-hydrazone tautomerism [3]. This method has a lot of deficiencies [4] of which the most serious is the impossibility to measure the permeation concentration of an experimental chemical and the possibility to measure the resistance of construction materials only for one chemical, therefore for sulphuric yperite.

With regard to the fact that the Army of the CR needs to measure the resistance of construction materials also for other substances from the group of so called industrial chemicals, the Research Technical Institute of Protection in Brno developed and in the army workplaces experimentally verified and introduced into laboratory practice the device PIEZOTEST [5,6,7,8,9]. This device, which uses for the detection of substances a QCM (Quartz Crystal Microbalance) sensor with a reversible polymer layer, is capable to detect very sensibly mass changes caused by the absorption of a sample substance in its polymer layer which are indicated by the change of operating frequency of a QCM sensor joined to an oscillatory circuit of the QCM detector. From the dependence of the change of the operation frequency of the QCM detector on the time we are able to determine the moment of the permeation of a substance through the construction material and at the same time also the velocity of the loss of protective properties of the tested material.

The detector itself is placed in a permeation cell whose scheme is provided in figure 1.

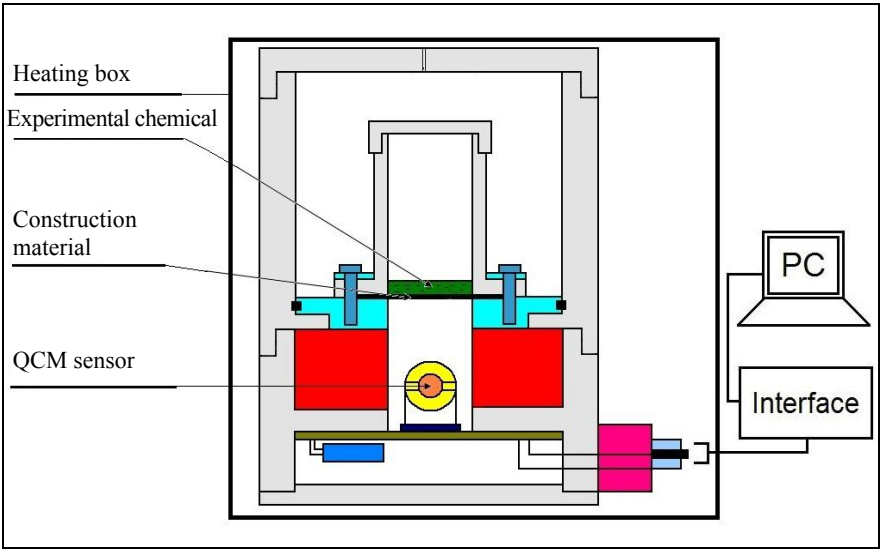


Fig. 1
Permeation cell of the PIEZOTEST device

During the measurement of the resistance itself, the detector is separated from the experimental chemical substance by means of the tested material. The substance, which went through the tested material and through transport processes permeated to the detector, is caught on a polymer layer laid on the detector, which causes the change of its operation frequency. The frequency signal is then conducted through a proper converter into a computer and is, by means of a program, recorded, elaborated and evaluated.

Also in case of this construction setting of the permeation cell it is not possible from the change of the operation frequency of the QCM detector to determine the permeated amount of an experimental chemical substance. Solving this problem proved to be the crucial one for other experimental work and also for covering the criteria determined by the norm CSN EN ISO 6529 related to commercial requirements for testing of construction materials together with potential determination of a toxicological impact of the dermal exposition due to the permeated amount of a harmful substance on a user of a protective garment.

2. SOLUTION OF PERMEATION CELL CALIBRATION AND TRANSPORT OF EXPERIMENTAL CHEMICAL INTO QCM DETECTOR

With regard to high sensitivity of the QCM detector it was necessary to set requirements which should be taken into consideration to ensure the reproducible calibration of permeation cells. It was set out that:

- during the calibration there must be the possibility to dose a small amount of the experimental chemical in a minimal number of five doses for designing a calibration curve;
- dosing must be feasible from the viewpoint of applied instruments and calibration methodology, achievable so that it might be used both in stationary and automobile laboratories with applied protective tools;
- calibration must be highly reproducible and the values dispersion must be minimal and comparable with analytical methods regardless the fact that it is not the analytical determination;
- during the calibration a suitable substance dispersion must be ensured in the form of vapors in the measuring space of the QCM detector, therefore it means the transition from a dosed liquid phase to a gaseous one;
- calibration appliances must be universal for all permeation cells without the necessity of additional adjustments.

After the analysis of available dose appliances and tools regarding the specification of permeation cells, the most suitable proved to be the micro-syringe HAMILTON 7001N PST 2 (sharp needle) which ensures sufficient accuracy for calibration purposes. For the calibration, with regard to the sensitiveness of the detector, the micro-syringe of the total volume l,0 μl with the option to dose per 0,001 μl was chosen.

The choice of the HAMILTON micro-syringe crucially influenced the construction of a calibration extender. The following requirements were specified for its construction:

- the construction of a calibration extender must enable a repetitive dosing of the experimental chemical under exactly specified geometric conditions so that the release of a chemical into the space of the QCM detector might occur and the detector might not be damaged;
- the calibration extender must be constructed in the way which ensures high tightness of the system during the dosing of the experimental chemical and the occurring vapors must not release outside the measuring space of the QCM detector.

Following these requirements, the calibration extender was produced from Teflon, therefore from the same material as the body of the permeation cell. Calibration extender was made in the shape of a cylinder whose length was by 0.5 mm shorter than the length of the micro-syringe HAMILTON needle. In order to insert the syringe needle, the opening of a 0.8 diameter was drilled into the

center of a cylinder. The outside diameter of a cylinder was the same as the outside diameter of a fragment of the permeation cell designed for the dosing of a chemical (fig. 2). The segment of a calibration extender determined for the insertion into the permeation cell was adapted by lathing to a relevant diameter. On this part, about 2 mm from the end, the trench for the insertion of chemically resistant sealing of VITON material was lathed in order to perfectly seal the space of the QCM detector and prevent the release of vapors of the experimental chemical from the QCM detector space.

Apart from the dosing of the experimental chemical, it was necessary to sort out also its effective transfer into the form of vapors and at the same time prevent potential dropping of a chemical on the QCM detector. The solution was to put on the spot of the tested material an appropriate membrane which would enable to suck the liquid pressed up from the HAMILTON syringe, expand its area for evaporation and enable its efficient evaporation. Finally, from a wide range of materials, a thin polyester fabric without adaptation was chosen. It abounds in high chemical resistance and covers determined requirements for the evaporation of experimental chemicals.

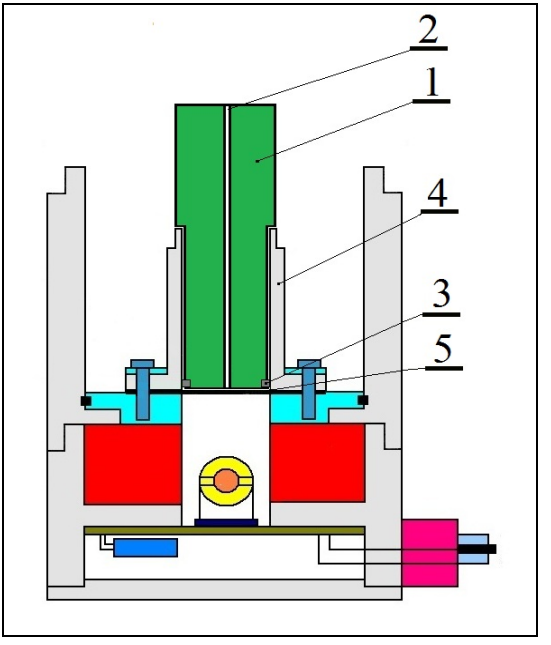


Fig. 2
Permeation cell with inserted calibration extender

1 – calibration extender, 2 – opening for insertion of HAMILTON micro-syringe needle, 3 – sealing, 4 – dosing space of permeation cell, 5 – evaporation fabric

The calibration itself confirmed the appropriate construction of the extender. Calibration extender enabled feasible insertion of the HAMILTON syringe needle. Reducing the length of the extender by 0.5 mm against the needle enabled the penetration of its spike into the polypropylene fabric and after the dosing of the experimental chemical it dispersed on the fabric and subsequently evaporated into the space of the QCM detector. It was possible to use the extender with any permeation cell.

Since it was necessary to keep the same temperature conditions during the calibration as during the measuring, it was crucial to ensure the heating of the permeation cell in the course of calibration. The biological incubator, which is used to ensure the heating of permeation cells in the course of the measurements of chemical resistance of construction materials, proved to be inappropriate due to the escape of the heat from the heated space. Therefore, the water thermostat U 15 (VEB MLV Prüfdaräte-Werk/Site Freital, Germany) was used as the source of the heat. The former plate cover was substituted by the plate cover made from organic glass (figure 3).

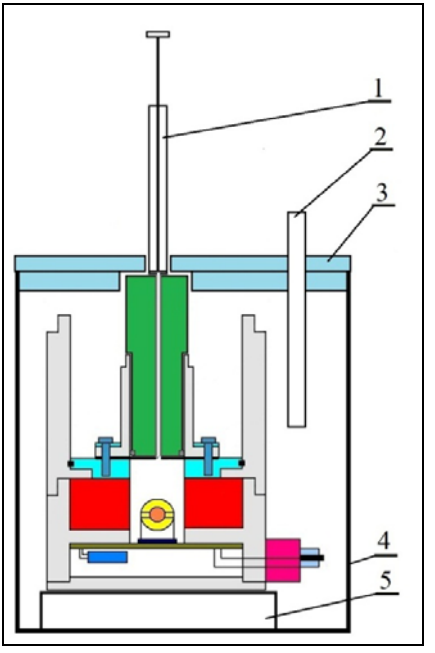


Fig. 3
Heating of the cell during the calibration of the permeation cell

1 – micro-syringe HAMILTON,
2 – sensor for the measurement of the temperature of the PIEZOTEST device,
3 – plate cover, 4 – heated container of water thermostat,
5 – pad adjusting the height of the permeation cell with regard to the cover of the thermostat

The cover was made by gluing two layers. The opening was made in the lower layer which enabled the insertion of a calibration extender and delimitated this way the position of the permeation cell for calibration. Above it, on the spot responding to its center, the opening was drilled and this enabled to insert the HAMILTON micro-syringe. Another opening in the cover was drilled in order to insert the sensor for the measurement of the temperature of the PIEZOTEST device so that it was possible to record the temperature during which the calibration proceeded. The height of the permeation container in the thermostat was adjusted using the pad.

The adjustment of the PIEZOTEST device for the calibration proved to be suitable. The calibration of the devices for a wide range of chemicals with excellent results was accomplished. In figure 4 you can see the results of the calibration for cyclohexane, n-octane, 1,6-dichlorhexane and benzylamine. From figure 4 it is obvious that the calibration curves have almost a linear course which is documented by high values of reliability within the frame of the performed linear regressive analysis.

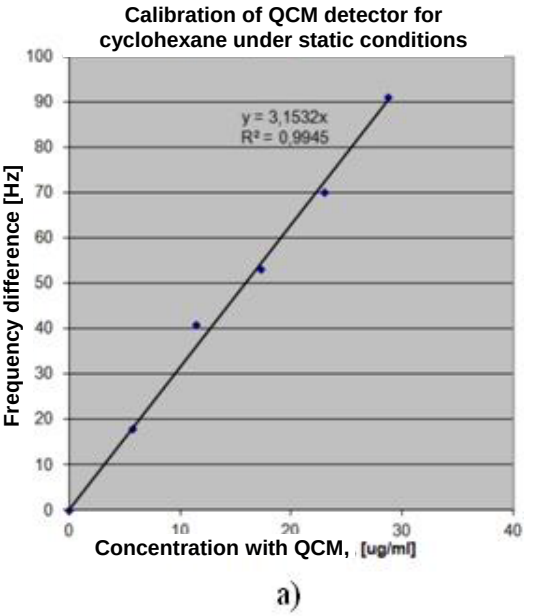
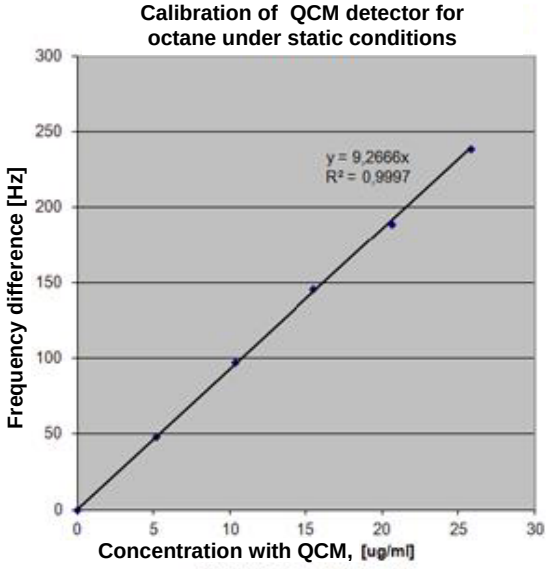
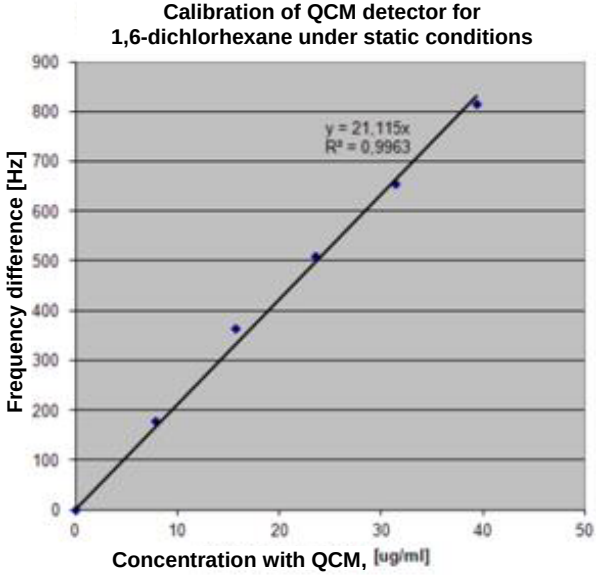


Fig. 4
Calibration curves for selected chemicals

a) cyclohexane



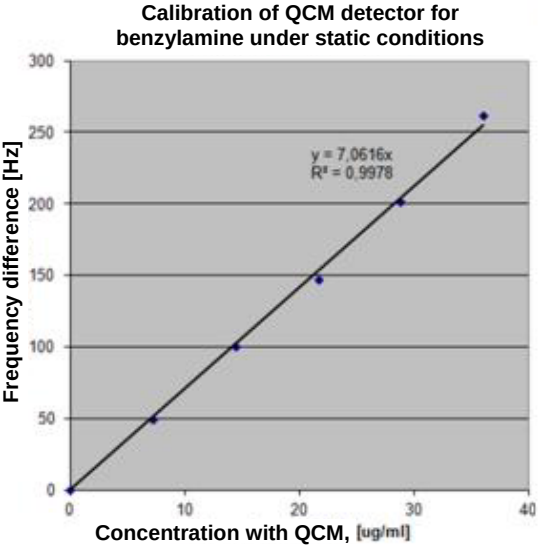
b)



c)

Fig. 4
Calibration curves for selected chemicals

b) n-octane; c) 1,6-dichlorhexane;



d)

Fig. 4
Calibration curves for selected chemicals

d) benzylamine

CONCLUSION

The calibration extender expanded the possibilities of the application of the PIEZOTEST device. Especially the possibility of the reading of penetration concentrations and their subsequent application for the estimate of toxicological effects of the observed chemical will enable to determine in a more quality way the times of resistance of means for personal protection. According to the dependence of the permeated amount of the experimental chemical on time, it will be possible to determine limiting time line of application of protective means in a contaminated area, therefore under the conditions when the toxic chemical affects the whole space of the means of personal protection.

Résumé

The measurement of construction materials resistance against toxic chemicals of concern is highly important not only from the user´s point of view but also from the commercial one. In both approaches it is necessary to differentiate the amount of toxic chemicals of concern permeating through protective materials.

We need to know the permeation of the exact amount of a toxic chemical through the material for the assessment of the protective quality in order to make comparisons from the user´s point of view either using toxicological characteristic of a toxic chemical permeated through barrier material, or determining the maximal amount of a toxic chemical which is still allowable to permeate.

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