Military Medical Science Letters

Mil. Med. Sci. Lett. (Voj. Zdrav. Listy) 2012, vol. 81(3), p. 113-118
ISSN 0372-7025
DOI: 10.31482/mmsl.2012.017

REVIEW ARTICLE

POSSIBILITIES OF THE QCM METHOD EMPLOYMENT TO DETERMINATION OF TOXIC COMPOUND CONCENTRATION IN DEPENDENCE OF BARRIER MATERIALS RESISTANCE

Pavel Otrisal✉, **Stanislav Florus**

NBC Defence Institute of the University of Defence, Vyskov, Czech Republic

Received 10th May 2012.
Revised 27th August 2012.
Published 7th September 2012.

Summary

This paper points to some aspects of possible usage of a QCM method within a set of toxic compounds permeated concentration based on a permeation curves rate and after underdone calibration of a measurement system. Presented assesses can be used not only in favour of the Czech Armed Forces Chemical Corps specialists but subsequently also in favour of personnel protection for those working in an area with toxic compounds appearance.

Key words: QCM sensor; calibration; toxic compound; Weapons of Mass Destruction; Chemical Corps; Czech Armed Forces

INTRODUCTION

In recent time big importance to improvement and indemnity of quality protection of deployed forces against inhalant toxicity has been devoted. This one is connected with development of breathing organs protective devices. Currently there exist some databases which are constructed for the most frequent (and the riskiest) form of exposition, thus inhalant exposition, [1]. Sufficient attention has not been paid to protection against percutaneous toxicity, thus to development of body surface protection, mainly that which is designated to specialists´ isolative protection. Specially produced databases designated for the risk and danger judgment for dermal exposition are not available in current time. It is necessary to introduce both forms of expositions – inhalant and dermal - which have one common important characteristic. This one is a direct entrance of chemical compounds into systematic circulation (and to aimed organs/tissues) without the first detoxicating passage with help of a liver. Contrary to this the liver plays a very important role in a case of per oral exposition. From these reasons it is possible to consider a certain analogy of mechanism of additivity and supra-additivity [2].

✉ University of Defence, NBC Defence Institute, Sídliště V. Nejedlého 691, 682 01 Vyškov, Czech Republic
Pavel.Otrisal@unob.cz
+420 973452335
+420 973452330

1. PROBLEMS OF PERMEATION AND DIFFUSION AND THEIR RELATIONSHIP TO DETERMINATION OF PERMEATED TOXIC COMPOUND CONCENTRATION THROUGH BARRIER MATERIALS

With the current study of protective properties of the isolative protective garment OPCH-05, which is introduced in the Czech Armed Forces (CAF) and which has been conducted at the NBC Defence Institute of the University of Defence, it has been found that ensuring of quality specialists´ isolative protection involves a number of problematic aspects which is necessary to work with in the future. One of the most important problems is toxic compounds permeation through barrier materials based on butyl-rubber. These materials are used as basic constructive materials of protective garments of OPCH-05. The second problem is determination of particular concentrations of permeated toxic compounds. Professionals from practice [3] claim that: "Evaluation of dermal exposition riskiness is an area considerably neglectful in regulation toxicology (industrial hygiene) at present time". Currently some data is available. Nonetheless, in no case we can speak about a general possibility of an easy access to it. Travníčková [4] said that particular values of dangerous concentrations are found ad hoc in hygienic practice, thus only on demand. These values are found in mutual cooperation of an applicant and the National Institute of Public Health. It is clear that a systematic access to introduced problems is missing. It means that each solution would be potentially very important.

The issue of permeation, thus the transportation of molecules of substances through biological materials under the influence of concentration gradient without the excitement has already been devoted to Thomas Graham in 1829. At that time he watched the gradual supercharging of pigs´ bladders with the help of detection of escaping CO_2 [5]. The author observed significant phenomena that characterize the permeation of gases. It was noted that it is possible to obtain various transport parameters and constants of barrier materials that do not depend on temperature, pressure and type of permeated gases. Knowledge of basic material properties allows the application of established methods of study of protective properties of constructive materials used to produce garments of an isolative type, where a more accurate description of transportation of mass is important.

The basic and characteristic process, by which penetration of toxic substances through a barrier layer of protective clothing can be described, is diffusion which is closely linked to the permeation process. For the case of isolative garments without ventilation, Slabotínský states that "chemicals can penetrate through intact and tight garments only by the slowest process, thus by diffusion" [6]. It does not take place, however, as the first process, but it builds on the sorption processes, including absorption, adsorption and processes which are usually accompanied by a process of exsorption and desorption [7,8]. Diffusion belongs to adsorption processes taking place between liquid and solid phases, thus between test chemicals (toxic substances) and tested isolative protective folio of the protective garment. Efficiency, effectiveness and importance of adsorption, however, always depend on the pore size of the researched surface which it runs on. The surface of the polymer folio formed by a mixture of butyl rubber polymer is insignificant in terms of porosity and almost negligible compared to, for example, the surface of activated carbon porosity. It is typical for all materials used to protect people against the effects of gases and vapors of toxic substances that they manifest a significant influence of permeation, which is esential for evaluation of airtightness of barrier materials [9].

2. GENERAL INTRODUCTION OF QCM DETECTION

Historical development of quartz resonant detectors (piezosensors) started by using quartz resonators as a time base for frequency regulation of time duration in the quartz clock. High reliability and stability of quartz oscillators is based on stability of resonant oscillations of a properly structured single quartz crystal. It is typical that saving a small amount of material on the surface of the quartz crystal microbalance (Quartz Crystal Microbalance - QCM) reduces its resonant frequency. Gravimetric use of QCM sensors is based on the change of basic oscillatory frequency f_0 by adsorption or absorption of molecules from the surrounding gas phase. In the simplest case, this phenomenon can be described by Sauerbray equation: [10]

$$\Delta f = -f_0^2 . \frac{c_f}{A_k} . \Delta m, \quad (1)$$

where Δm is mass increasing, Δf is frequency decreasing, A_k is a size of crystal´s layered surface, f_0 is basic oscillatory frequency of the crystal, c_f is mass sensitivity.

Sensitivity c_f may reach about 2.3 x 10^{-10} $g.m^{-2}$ by a quartz resonator operating in vibratory-shear mode mass. For a resonator with the basic frequency f_0 = 10 MHz, the detection limit of the detector is equaled to a nano-gram level [11,12]. Obšel and Dvořáková explain that with the employment of formula (1) it is possible to count a unit addition of mass Δm which - in case of a used QCM detector – has reached approximately the value of 6,8 $ng.cm^{-2}$. Formula (1) also shows that a relative change of frequency is proportional to a mass change on detector´s surface (quartz).

$$\frac{\Delta f}{f_0} = -\frac{\Delta m}{m}. \qquad \textbf{(2)}$$

From equation (2) it is clear that the weight limit depends on the weight of the crystal m. The thickness of the AT cut crystal is decisive for a working frequency of the QCM detector with a polymer layer, but this rate cannot exceed 20 MHz. This frequency limits the detection limit on the maximum value of 0.1 $ng.mm^{-2}$ of a detector (crystal) active area.

3. METHOD OF DATA EVALUATION

To find out a protective characteristic, a PIEZOTEST device has been employed (Figure 1). This one has been developed at the Military Technical Institute of Protection in Brno. For detection of permeated toxic compounds´ molecules the above described detector has been used.

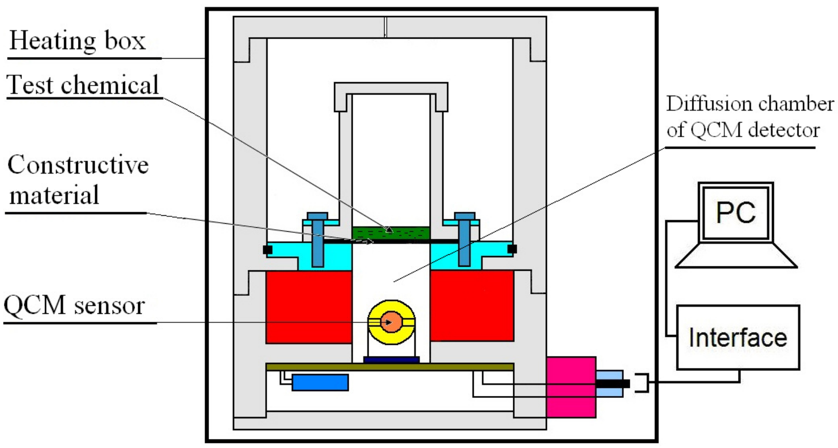

Figure 1. The scheme of PIEZOTEST device working on QCM detection principle.

Equation (1) shows that precisely measured physical quantity is the frequency. A very important advantage of using detectors is the possibility of providing outputs in the form of digitally measurable values, which need not be further transferred. After recomputation of a frequency change (Δf) of a detector on concentration it is possible to construct dependence of the concentration-time and then deduct the value of the breakthrough time of the material time particular for the test chemical. For a rapid evaluation of the researched material resistance, a curve showing dependence of the QCM detector working frequency increase on time can be constructed. Through the extension of the linear dependence and its intersection with the time axis, the approximate value of breakthrough time, so called lag time (t_l), for a particular chemical, constructive material and temperature of measurement, can be obtained (Figure 2). Lag time basically determines the beginning of a steady state of permeation rate of chemical substance through barrier material. The slope of the linear part of the curve indicates the speed with which construction material loses its protective properties, thus speed at which the concentration of toxic compounds in the diffusion chamber of the QCM detector (Figure 1) increases. Isolative protective folio separates toxic liquid phase of test chemical.

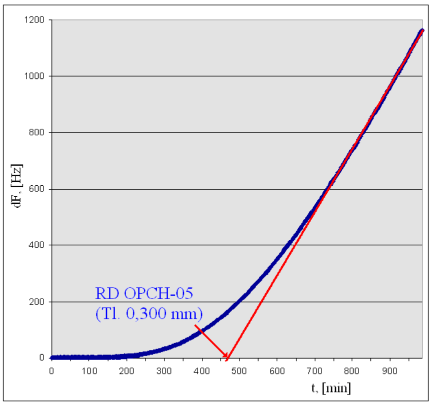

Figure 2. The scheme of quick evaluation of constructive materials resistance from dependence of QCM detector working frequency on time with help of t_l.

To calculate Δf on the permeated test chemical amount (its concentration), calibrations of QCM detectors have been performed. From calibration curves, conversion equations of calibration have been read, respectively equations of regression with the help of MS Excel application. In this application, a graph of dependency of Δf increase on a particular amount (concentration) of a test chemical has been constructed. Gained data have been used for concentration of particular chemical substance determination in the diffusion chamber of permeation cell (by QCM sensor) which has been constructed for chemical resistance measurement in static conditions (close permeation loop) at the moment of reaching the time concerning t_l in accordance to the formula (3):

$$c_{QCM} = \frac{\Delta f}{y} \tag{3}$$

where c_{QCM} is concentration in the diffusion chamber of the permeation cell at the moment of t_l achievement, Δf expresses the QCM detector working frequency increasing at the time of reaching t_l, y is a founded value of the regression equation based on linear dependency of the curve Δf on c in a framework of QCM detector calibration in static conditions. A particular value of Δf has been found by constructing a tangent line vertical to x axis (time increasing) at the moment of reaching t_l. This line has been intersected with a curve of duration of Δf increasing at the time of exposition. The value of Δf has been read from y axis as is shown in Figure 3.

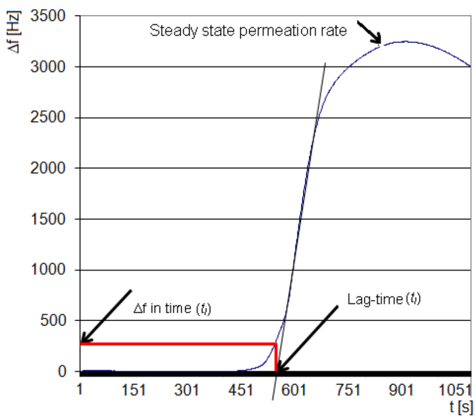

Figure 3. The way of reading Δf at the time of reaching t_l.

Based on the executed QCM detectors calibration, it is possible to obtain data on concentrations of toxic compounds at the time of achieving not only t_l, but also at the moment of a complete loss of isolative protective garment protective properties, thus when a steady state permeation rate is achieved. Achieving this state is characterized by high levels of toxic compound permeation into the space of an undergarment area of the isolative protective garment, which a user with no protective clothing or without it is exposed to with virtually the same exposure of the toxic substance; therefore, the isolative protective garment will be fully functionless. Methods of QCM detection, however, are not analytical methods, but the methods of characteristics to identify protective barrier material. It is certainly possible to use these methods to determine concentrations of toxic substances permeated into the isolative space of the undergarment area of protective device, thus to the space which is very close to the user´s skin.

Despite the fact that mass contamination of the isolative protective garment, which was characterized by permeation of toxic compounds through the whole surface of the isolative protective garment, is not expected, in principle, it is very important to set the maximum amount of time after which the user will be reliably protected from the effects of toxic compounds permeated in places where contamination can occur with high probability. As already stated, the information is currently either lacking or is only available for a selected range of toxic substances which are mostly used in manufacturing technology and practice. Operative time determination of the protective effect of the isolative protective garment provided by the knowledge of specific concentrations of toxic compounds that are harmful for a user´s organism is very important. Aside from the fact that the user of the protective isolative garment is significantly limited by the length of the wear from the viewpoint of the occurrence of heat shock-related to dehydration of the organism and the possibility that there are practically no limit concentrations of toxic substances and specification of the characteristic effects on the human´s organism, the possibility of operational and almost immediate determination of time of the protective effect seems to be very beneficial. A norm which deals with principles and description of methods concerning measurement of dermal exposition at workplaces, denoted as ČSN P CEN/TS 15279 (83 3618) „Workplace exposure - Measurement of dermal exposure - Principles and methods" from 2006, provides a guide to common used procedures of dermal exposition measurement, introduces their advantages and disadvantages and even restrictions and ways how specific harmful substances can be evaluated in specific conditions. This specification is intended to allow a user an access to methods for assessing dermal exposure in order to adopt a consistent approach, to validate the method and to provide a framework for evaluation of the method. The specification describes demands needed for evaluation of a taken method. This also shows the methods that are consistent with those requirements. To implement this standard Fuchs [13] states that: "It would be appropriate that the standard methods described have been verified in practice." This statement can be understood as a challenge for research on the appropriateness of the use of QCM detection methods for meeting the requirements of the above mentioned norm.

CONCLUSION

Even today, when material and usable chemistry has reached a very high level, it cannot be reliably said that there is a perfect barrier material that would absolutely protect against the effects of toxic substances. Processes of permeation associated with diffusion occur independently of the man´s will and are linked to an intrinsic characteristic of materials forming a barrier between phase interfaces of considered substances. Despite the fact that in current time the study of protective properties of isolation protection devices is devoted a higher attention in military practice, the obtained outputs are still waiting for their extensive practical application. A possibility of the QCM detection usage to determine the maximum period during which the isolative protective garment will reliably protect from the effects of toxic substances and therefore will reliably protect the health of the user before the intoxication of the organism, seems to be real. Any increase in the reliability of estimates of additive and interaction potential of toxic substances or their mixtures (additivity, supra-additivity, infra-additivity) can facilitate decision making in the field of occupational hygiene, industrial toxicology and occupational medicine. It can be supposed that development of mutual cooperation between NBC Defence Institute and specialized army and civilian workplaces it will be to employ QCM detection method to the aim research of under interest problems.

ACKNOWLEDGEMENT

The work presented in this paper has been supported by the Ministry of Defence of the Czech Republic (research project No. PRO 9079301010).

REFERENCES

1. FIALA, Z. et al. Evaluation of potential activity and interaction in chemical compounds mixtures in working environment (in Czech). 1. vyd. Brno : MSD, **2011**. 133s. ISBN 978-80-7392-180-4.
2. FIALA, Z. Personnel communication. 13.3.2012.
3. See e.g. FIALA, Z. < Fiala@lfhk.cuni.cz >. Possibilities of undergarment cancentration determination. OTŘÍSAL, Pavel Pavel.Otrisal@unob.cz. **2012**-03-26 7:16. [cit. 2012-04-13].
4. TRÁVNÍČKOVÁ, Z. Personnel communication. 3.2.**2011**.
5. DHINGRA, Singh, Sukhtej. Mixed gas transport study through polymeric membranes: a novel technique. [Dissertation work]. Virginia, Blacksburg : **1997**. 172 s.
6. SLABOTINSKÝ J., BRÁDKA, S. Personnel protection within chemical and biological threat (in Czech). 1. vyd. Ostrava : Sdružení požárního a bezpečnostního inženýrství v Ostravě, **2006**. 109 s. ISBN 80-86634-93-0.
7. CHOVANCOVÁ, L. Chemical technique: diffusion operations (in Czech). 1. vyd. Havlíčkův Brod : nakladatelství FRAGMENT, **1988**. 84 s. ISBN 80-7200-214-7.
8. ROMANO, A., James, LUKEY, E. Brian, SALEM, Harry. Chemical warfare agents: Chemistry, Pharmacology, Toxicology and Therapeutics.. 2. vyd. New York : Taylor & Francis Group, **2010**. 723 s. ISBN 1-4200-4661-6.
9. HAUFFE, Karl, MORRISON, S., Roy. Adsorption: Eine Einführung in die Probleme der Adsorption. 1. vyd. Berlín : Walter de Gruyter, **1973**. 190 s. ISBN 3-11-003958-3.
10. OBŠEL, V., DVOŘÁKOVÁ, J. Research of possibilities of applications nanotechnology in chemical protection – nanostructured barrier materials and testing of their resistance against toxic compounds permeation. [Technical message of the project of NANOMATERIÁLY in year 2009]. VOP-026 Šternberk, s.p. divize VTÚO Brno. Brno : **2010**. 118 s.
11. TAJITSU, Y. Piezoelectricity of Ferroelectret Film. In Conference Proceeding of the International Conference PERMEA 2009. 1. vydání. Praha : Institute of Macromolecular Chemistry AS CR, **2009**, 7.-11.6.2009, p. 62. ISBN 978-80-85009-58-3.
12. TOKO, Kiyoshi. Biomimetic Sensor Technology. 1. vyd. West Nyack : Cambridge University Press, **2000**. 223 s. ISBN 978-0-52159-342-7.
13. Web pages of The National Institute of Public Health. [online]. c2012. FUCHS, A., WALDMAN, M. Possibilities of Czech technical norms within identification of chemical risks on workplaces (in Czech). [quated **2012**-04-13]. Availabla from: <http://www.szu.cz/tema/pracovni-prostredi/moznosti-vyuziti-ceskych-technickych-norem-pri-identifikaci>.