Possibilities of Usage a Piezoelectric Detector to Measure the Breakthrough Time of Protective Materials

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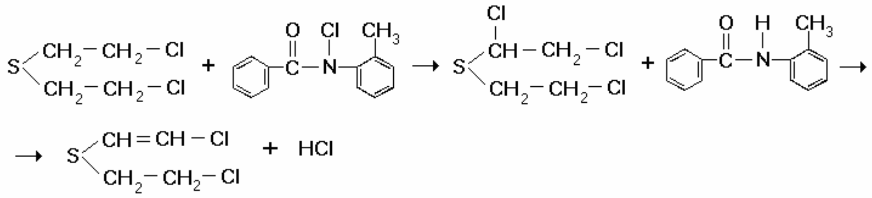
Introduction

The method called MIKROTEST is used in the Army of the Czech Republic as a primary method to measure the breakthrough time of chemical agents. This method uses hygroscopic cellulose paper colored with Congo red (pH-indicator) and after drying activated with *N*-chlor-*N*-(2-tolyl)benzamide (CNITI-8) as an indicator of sulfur mustard penetration. The principle of indication is based upon the reaction of CNITI-8 amide with sulfur mustard which releases hydrogen chloride converting the alkali form of an acidobasic indicator to the acid form, subsequently the Congo red form is converted to the blue form using azo-hydrazone tautometry.



The indicator paper is in direct contact with a measured insulating foil and the change of color to blue occurs at the point of chemical agent penetration. The moment of penetration of the chemical agent threshold amount (0.005 mg.cm^{-2}) is signaled by the first perceivable blue spot with a diameter of approximately 1 mm (Fig.1).

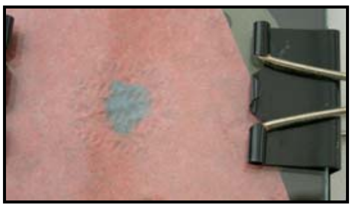


Fig. 1 A blue spot on the indication paper created after the sulfur mustard penetration through a sample of material

The emergence of the blue spot is detected subjectively. The process of turning blue indicates a pH change in the range of 4 through 5. The change in coloration is initiated by hydrogen chloride in a concentration of about 1.10^{-3} $mol.dm^{-3}$, which in theory corresponds to the same sulfur mustard concentration. An advantage of this method is the quick reaction response of sulfur mustard with the indicator. The measurement is carried out at the temperature of $30^{o}C$.

The advantages of the MIKROTEST method are as follows:

- high sensitivity;
- small consumption of a chemical agent (20 μl);
- material testing using an actual chemical agent – sulfur mustard;
- simplicity of the method which does not demand complicated equipment; and
- minor requirements for education and training of the personnel performing material testing.

The disadvantages of the MIKROTEST method are as follows:

- necessity of subjective observation throughout the experiment;
- high spread of results;
- possibility of varying assessments by different observers who evaluate the penetration moment of sulfur mustard identified by the emergence of a blue spot;
- possibility of bias in results as a consequence of sample twist due to its swelling;
- possibility of complete failure of the two-stage chemical reaction necessary to indicate sulfur mustard penetration to the back side of a sample in consequence of a secondary chemical reaction with the sample;
- necessity of laboratory preparation of CNITI-8 amide which is not commonly available on the market; and
- possibility to detect the breakthrough time for sulfur mustard only.

The MIKROTEST method limitation can be compensated for using both new equipment and the method called PIEZOTEST. To detect the penetration of harmful substances this method uses a piezoelectric crystal detector having a polymeric layer which works as an extremely sensitive microbalance.

Quartz Crystal Microbalance (QCM) is a piezoelectric device which is able to measure changes in mass with a nanogram accuracy very sensitively. With the application of a high-frequency electric field using metal electrodes placed on both sides of a circular disc of AT- cut of quartz crystal, the crystal oscillates in a mechanically resonant shear mode. The mass sensitivity of oscillatory frequency depends on a sum of the crystal mass, electrodes used and construction materials on their surface (Fig. 2). An application of a suitable detection layer on the surface of electrodes enables temporary or permanent bonding of the crystal and a test substance causing a detectable change of the crystal mass. For QCM detectors it is typical to use an AT-cut of quartz crystal having the basic frequency of 9 MHz which is easily changeable with the result that 1 ng of analyte which sticks to the surface of the crystal detection layer can be detected immediately as the decrease of crystal oscillatory frequency of 1 Hz.

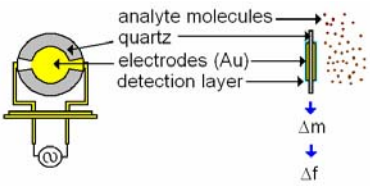


Fig. 2 QCM sensor working principle

A sample of the insulating protective foil tested is located in a teflon permeation cell (Fig. 3). The sample of the insulating protective foil divides the permeation cell into two parts hermetically - the part where contamination caused by a harmful substance takes place and the part where a reversible QCM detector with a polymeric layer is situated. The harmful substance, which has penetrated the protective foil and the concentration of which increases in a closed space around the detector, proceeds with diffusion processes, the speed of which is in the range of $cm.min^{-1}$ in relation to the measuring crystal. The harmful substance is caught in the detector polymeric layer, which causes the change of its working frequency. After that, a detector frequency signal is fed into a computer through a suitable interface where it is recorded, processed and assessed using software developed specially for this purpose.

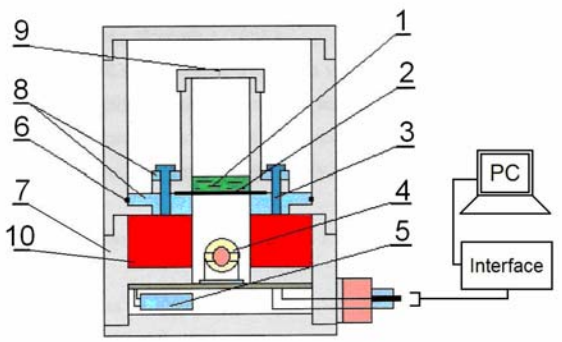


Fig. 3: A schema of the PIEZOTEST device permeation cell

1 – test substance, 2 – tested material, 3 – tightening screws,
4 – measuring crystal,5 – reference crystal, 6 – tightening ring,
7 – body of permeation cell, 8 – collars, 9 – air hole, 10 – teflon pad

A permeation curve, i.e. the dependence of detector frequency change on time, is the result of the measurement. Since permeation is dependent on the measurement temperature, the permeation cell is tempered at the demanded temperature during the test.

The advantages of this method are as follows:

- objectivity of measurement;
- small consumption of testing substances - 300 μl;
- automatic measurement of observed values after the preparation and initiation of the measuring device;
- clear assessment of measurement results, i.e. the dependence of the working frequency change on the measurement time (Fig. 4);
- possibility of measuring breakthrough times for a wide spectrum of special-interest substances;
- good measurement repeatability;
- easily managed method during experimentation;
- possibility of measurement of both hermetical and non-hermetical materials without the necessity of device adjustment; and
- possibility of using various types of permeation cells in dependence on the character of the measured material.

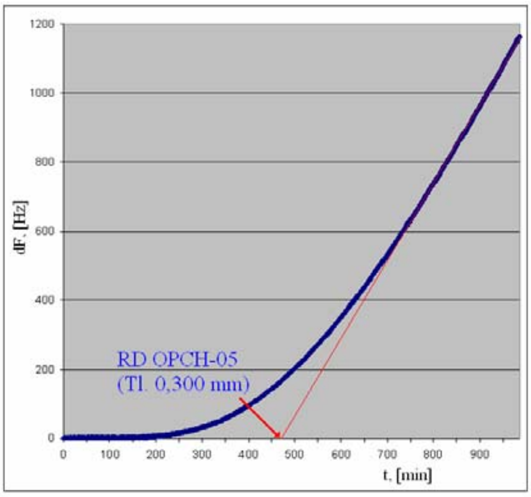


Fig. 4 Graphical assessment of the insulating protective foil breakthrough time measured by the PIEZOTEST method

The disadvantages of this method are as follows:

- longer measurement time caused by the need to gain the course of the dependence of working frequency change on time in order to be able to determine the time of substance penetration to the back side of the insulating protective folio unambiguously; and

- possibility of QCM detector destruction due to careless handling of the permeation cell or during work with some substances, e.g. strong mineral acids which, in high concentration, would penetrate a part of the permeation cell.

Conclusion

Both methods to measure breakthrough times have their own advantages and disadvantages. The PIEZOTEST method appears to be considerably preferable for practical measurement and for its universality, mainly with very resistant materials, the breakthrough times of which are long. The PIEZOTEST method enables monitoring the process of permeation of harmful substances, assessing permeation dynamics and comparing the relationship between a chemical substance and material tested. With a permeation cell adjusted it is possible to detect the permeation of vapors through construction materials, to test the resistance of powdered layers of various characters or to detect the resistance of construction materials in dynamic conditions.