Testing Methods of Assessment for the Chemical Resistance of Insulating Materials Against the Effect of Selected Acids

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The Czech Armed Forces´ soldiers of all specializations and mainly the chemical corps´specialist are prepared for task fulfillment in military and non-military operations within those a real threat of weapons of mass destruction employment and, occasionally, the real danger of toxic industrial materials leakage is present. They can solve problems caused by acids leakage in contaminated areas mainly during task fulfillment in non-military operations on the Czech Republic territory in cooperation with Fire Rescue Brigades´ chemical specialists. Individual protective equipment which is established in the Czech Armed Forces were neither design for this purpose and, moreover, nor tested and thus there is no real data concerning their chemical resistivity. In recent time, some methods have been introduced into the Czech Armed Forces environment. They are useful for determination of chemical resistivity of barrier materials against toxic compounds detectable with acid-basic (colorimetric) methods and conductometric ones. The paper deals with the possibility of using the presented methods and compares the suitability of their application in relation to the protective garments designated for the Czech Armed Forces members´ body surface.

Key words: isolative protective material, breakthrough time, acid, method, MINITEST, KONDUKTOTEST, MIKROTEST, chemical resistivity

The chemical industry in the Czech Republic (CR) has a long tradition and can be considered as relatively safe. Despite the fact that a level of regulatory and security measures are strictly regulated in the CR by laws and decrees that are very closely related to the rules of the European Union, it is not possible to exclude situations related to the leakage of toxic hazardous substances not only for the population but also for the environment.

The CR Armed Forces (AF) are systematically and in the long term prepared not only for the fulfilment of tasks in military operations conducted outside the territory of the CR, but also for non-military operations taking place within the state [1]. The declared commitments of the CR AF in relation with assistance operations in support of the Integrated Rescue System (IRS) may be carried out for rescue work in disasters or in other serious situations endangering lives, health, property values or the environment if administrative authorities, local authorities and the basic components of the IRS cannot provide rescue work by their own forces [2-7]. It follows that all soldiers, without distinction of a branch and membership to a unit (formation, brigade level formation or facility), can be used in cases of disturbance of industrial infrastructure objectives [8-11]. In practice, this means that they can solve the problems associated with eliminating the consequences of contamination caused by leaks of toxic industrial chemicals, including inorganic and organic acids. The fulfilment of this type of tasks was not a standard requirement for the CR AF before the effectiveness of the Crisis Law Package from the year 2000 and it is therefore not possible to assume the protective properties of the isolative protective materials used in fact for the construction of the individual protective equipment (IPE) [12-18].

From the point of view of general properties of polymeric materials used as a constructive basis for the production of body surface protection garments introduced in the Czech Armed Forces (CAF), it is possible to assume a high level of protection against the effects of the liquid phases of the test chemicals used. However, the assumptions applicable for pure polymeric materials may not be the same as that provided with real protection in the case of polymer mixtures used for the production of IPE under conditions of long-term exposure to concentrated organic and inorganic acids [19-23].

At present, the standard methods for testing and detection of the barrier materials chemical resistance against the permeation of toxic substances are available in the CAF. Among the simplest and most user-demanding methods are those based on the chemical reaction of the permeated acid with an acid-base indicator embedded on the cellulosic carrier while monitoring a colour change on a detection layer. However, these ways of finding breakthrough time (BT) for chemically resistant barrier materials are relatively user-intensive from the point of view of the need to permanently monitor and record the moment of colour change of the indication layer, thus obtaining the response of the test chemical permeation through a tested material. For this reason, the methods of using the classic electro-physical or electrochemical analytical methods were introduced into the CAF. Their use, on the one hand, assumes a certain level of knowledge and safety of the service staff [24-26], but thanks to a sustainable and efficient management [27-33] which implements the semi-automatic data acquisition and recording system, they can apply modern methods of data evaluation, including their digitization [34-41].

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Name of the chemical	Specification, clearance	Mr	Producer (supplier)			
Acetic acid (CH ₃ COOH)	99 % p. a.	60.05	Penta, produced division Chrudim (CR)			
Bromocresol green	-	698.04	Lachema, national enterprice (n.e.) Brno (wCR)			
Bromophenol blue	-	669.99	Lachema, n.e. Brno (CR)			
Chloroacetic acid (HCl)	35 % p. a.	36.46	Penta, produced division Chrudim (CR)			
Congo red	-	696.68	Penta, produced division Chrudim (CR)			
Ethanol	clean	46.07	Penta, produced division Chrudim (CR)			
Formic acid (HCOOH)	85 % p. a.	46.03	Penta, produced division Chrudim (CR)			
Malachite green	-	364.92	Lachema, n.e. Brno (CR)			
Methyl orange	-	327.34	Lachema, n.e. Brno (CR)			
Methyl red	-	269.31	Merck-Schuchardt (SRN)			
Nitric acid (HNO ₃)			Lach-Ner, Ltd, Neratovice (CR)			
Orthophosphoric acid (H ₃ PO ₄)	85 % p. a.	98.00	Lach-Ner, Ltd, Neratovice (CR)			
Sulphuric acid (H ₂ SO ₄)	96 % p. a.	98.08	Lach-Ner, Ltd, Neratovice (CR)			

Table 1 SPECIFICATION OF USED CHEMICALS

Experimental part

Reagents

An overview and basic data on used chemicals are summarized in table 1.

Barrier materials

In order to determine the real BT the constructive materials of established IPE in the CAF have been used in the form of particular products:

-polyethylene (PE) with a flame retardant, which is the basic constructive material of the JP-75 anti-chemical kit; -polyethylene vinyl acetate (PEVA), which is used for production of a single-piece raincoat JP-90;

-butyl-rubber polymeric mixture (BPM) on both sides coated on a polyamide carrier fabric which is used for the production of OPCH-05 ventilated chemical protective garment:

-Tyvek textile with the aclar laminated film as a construction material for light decontamination suit TRF-4. It was used in a grey suit variant primarily designed to protect against the effects of organic compounds.

Apparatus

Cellulose Cosmetic Napkins Big Soft deluxe (MORACELL, Ltd, ZabCice, CR) with neutral leachate have been used to select the measurement indicator. Acid-base indicators have been prepared according to the CSN 68 4062 (684062) A norm [42]. A sprayer DESAGA SG1B (Desaga GmbH, Wiesloch, SRN) has been used for spraying solution of indicators onto cellulose wipes. Prepared wipes have been left for desiccation at the room temperature (fig. 1).



Fig. 1. Desiccation of prepared indicator layers

The MIKROTEST modified method (fig. 2) has been used to determine BT. The modification contented employment of MAULY 25 mm clamps to assure the tightness of the assembly. Preparations for the modified MINITEST [43-45] method using either a PVDF plate (fig. 3) or a rubber insert of the chemically resistant VITON (fig. 4) and the KONDUKTOTEST assembly, the principle of which is based on figure 5 have also been used. The Whatman paper

(Whatman International Ltd Maidstone, England) has been used as the indication layer for modified MIKROTEST method and modified MINITEST method.

Fig. 2. Modified MIKROTEST set: 1 - underlay glass, 2 - detection layer, 3 - tested material, 4 rubber mask with a round hole, 5 - cover glass, 6 - drop of tested chemical

Fig. 3. Modified MINITEST set using PVDF board (top view): 1 - underlying glass, 2 - indicator layer (Whatman impregnated paper with indicator solution), 3 - tested material, 4 - PVDF plate with 20 openings for test chemical sample deposition, 5 - cover glass



Fig. 4. Modified MINITEST set using a rubber-resistant VITON rubber insert (side view): 1 - cover glass, 2 - rubber insert of chemically resistant VITON, 3 - sample of tested material, 4 - Whatman impregnated paper with the indicator solution, 5 - base glass, 6 - test chemical

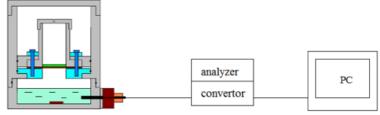


Fig. 5. The block diagram of the KONDUKTOTEST device within contamination of the sample of the tested material with the liquid phase of the tested chemical (acid)

Samples of the tested materials have been cut from the original footage with standard scissors or cut by hand hydraulic press (Polymertest, Zlin, CR) using a punch (MARBACH - CR, Ltd., Brno, CR). The thickness of the samples has been measured with a MITUTOYO thickness gauge (Mitutoyo Corporation, Kawasaki, Japan). Sets of the modified MIKROTEST device and the modified set MINITEST with samples of the tested materials have been

tempered throughout the whole measurement period in the biological incubator FRIOCEL 111 (BMT Medical Technology, Ltd., Brno, CR). The KONDUKTOTEST permeation cells have been tempered in a MINI incubator (GFL 4010, Gesellschaft für Laboratchnik mbH, D-30938 Burgwedel, Germany). A cordless screwdriver (Hitachi DB3DL, Hitachi, Japan) has been used to assemble the permeation cells of the KONDUKTOTEST device and a standard 3 mm ELLIX Allen key (Emil Lux GmbH, Wermelskirchen, Germany) has been used in order to fully tighten the whole set.

Methods of measurement The modified MIKROTEST method

The modified MIKROTEST method (fig. 1) is a simple, subjective, visual-colorimetric method, which is designated for the orientation determination of BT of tested materials. The detection layer is the Whatman paper impregnated with Congo red as a *pH* indicator. Permeated pairs of test chemicals convert the alkaline form of the *pH* indicator to the acid one, resulting in a colour change of the red-blue of the Congo red indicator. The colour change is observed and evaluated subjectively by an observer.

The modified MINITEST method

The MINITEST method is primarily designed to evaluate the resistance of barrier materials of textile type in the type of filtering protective suit against toxic substances vapor permeation. For the purpose of determination, the resistance of the flat isolated barrier materials, the set for liquid-phase of test chemical (figs. 3 and 4) has been used. Pairs of permeated test chemicals in the case of permeation processes or the liquid phase of the test chemical in case of destruction of the barrier material with the occurrence of penetration processes permeated through the tested material and caused a colour change of the indicator similarly to the MINITEST method.

KONDUKTOTEST method

The method and consequently the KONDUKTOTEST methodology is designed to determine the chemical resistance of porous and non-porous protective materials against permeation of volatile toxic substances with acidbase properties, including sulphur mustard, based on standard quantities such as permeation rate and cumulative amount. In static conditions, it is possible to determine the so-called lag-time from the course of increasing the concentration of dissociated ions in redistilled water and subsequently increasing the cumulative amount using the software GRYF-XBC8 Magic, which corresponds to BT for the purpose of rapid evaluation of the chemical resistance of the barrier materials. The permeation cell used a specially modified glass-carbon roller electrode to detect the change in specific conductivity.

Special software

A special software GRYF XBC8 Magic has been used to record and process obtained measured data using the KONDUKTOTEST method. This software is implemented as an extension of a standard computer. Measuring probes and XBC Magic Interface are part of a single device that is connected to a computer via a USB port. The interface XBC8 Magic is a device that converts a carbon-electrode signal to the computer. The software was used to calibrate the electrodes as well as to detect permeation of toxic substances by the KONDUKTOTEST method.

Working procedures

Selection of the indicator and preparation of the indicator layer for colorimetric measurement

Selected acid-base indicators were prepared according to the appropriate norm. The cellulosic napkin has been cut in half, swept for a few seconds in the appropriate indicator and then left to freeze dry by hanging it with a metal rod clip held in the stand (fig. 1). Dried indicating papers were stored in a Petri dish to protect them from the effects of chemicals in the laboratory environment. Similarly, indication layers have been prepared using Whatman paper. The functionality, response and colour intensity of the indicator papers have been tested for the concentration of saturated vapours of the test chemicals (about 0.2 cm above the acid level) and the gas phase at a distance of approximately 2 cm from the surface. The dried indicator papers have been cut to 70x70 mm or 130x160 mm depending on whether they have been designed for the MINITEST or MIKROTEST method and kept in the Petri dish

Measurement of resistance of construction materials by the modified MIKROTEST method

The tested material has been cut to 70x70 mm. Each sample has been measured in the centre with a thickness gauge. The impregnated indicating paper with the Congo red indicator has been placed on the base glass. A sample of the tested material has been placed directly on the indicating layer and covered with a rubber mask with a 20 mm diameter central hole into which 30µL of the test chemical (acid) was dispensed. The set has been fitted with a cover glass and closed with clamps. The sets (fig. 1) have been inserted into a biological indicator set at 30 °C so that the colour of the indicator layer on the underside of the set could be monitored while maintaining the condition of a horizontal position. From the time of dosing the test chemical the BT has been measured. The measurement has been stopped at the time of the test chemical permeation through the tested material. It has been indicated by changing the colour of the indicator layer from red to blue or after 480 minutes after acid deposition, even though the permeation of the test chemical through the tested material was not recorded.

Measurement of resistance of construction materials by the modified MINITEST method

The tested material has been cut at size of $130x\ 60\ mm$. Each sample has been measured with the thickness gauge at the location of the centre of the PVDF plate or a VITON insert. The Whatman paper impregnated with the Congo red has been placed on the base glass. A sample of the tested material has been placed on the indication layer. The material has been then covered with a PVDF plate or a VITON rubber liner of the same dimensions and a height of 3 mm with 20 round holes of 20 mm in diameter, into which have always been dispensed $30\ \mu L$ of the same test chemical. The set (figs. 3 and 4) has been covered with a cover glass and the whole set has been clamped. The rate of the measurement and measurement conditions have been the same as for the MIKROTEST method.

Measurement of resistance of construction materials by KONDUKTOTEST device

The samples of the protective foil have been punched out by a punch and the hydraulic press to a format for the permeation cell of the KONDUKTOTEST method. Each sample has been carefully measured in the centre on several places with the thickness gauge. Samples have been divided into group of 8 pieces so that each set of

samples has been characterized by the smallest deviation of the measured thickness. The KONDUKTOTEST device allows four samples to be measured at the same time, so 4 samples have been used for each material-acid measurement. In the case of results demonstrating the permeation of the test chemicals, other 4 samples from the set have been measured. A sample of the tested material has been inserted into the permeation cell. The cell was assembled in a conventional manner. A magnetic stirrer has been placed in 50 mL of redistilled water. After dosing 2 mL of the test chemical, the software GRYF-XBC8 Magic has been started on the evaluation device and the current permeation data have been collected and processed. During the measurement, permeation cells 1 and 2 have been conditioned at 30°C in the incubator MINI, while cells 3 and 4 have been left at normal laboratory temperature and hence they provided data about the BT corresponding to the temperature about 10 degrees lower.

After plotting the linear part of the change in permeation mass Q to time t or at 480 min after the start, the measurement has been stopped. The lag-time value has been subtracted from the linear part of the cumulative mass on a time dependent plot.

Results and discussions

Indicators selection and employment

Based on the tests conducted to verify suitability of different acid-base indicators used in measuring the resistance of construction barrier materials to acids, it was found that the Congo red and methyl orange indicators have been assessed as the most useful. Figure 6 shows the results of the indicator papers colouring before and after exposure to the test chemicals. Indicators of methyl red, bromophenol blue and bromocresol green have no longer been used for measurement because they were coloured in their acid form due to their sensitivity in a chemical laboratory environment.

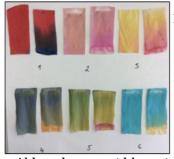


Fig. 6. Reaction of indicators to acid environment (right) compared to indicators in the laboratory environment (left): 1 - Congo red, 2 - methyl red, 3 - methyl orange, 4 - bromophenol blue, 5 - bromocresol green, 6 - malachite green

Although two acid-base indicators, Congo red and methyl-orange have been suitable for use in subsequent measurements, the Congo red indicator has been further used to provide the same measurement conditions and a clearer interpretation of the results, which determined a more pronounced colour difference when switching from base to acid form.

Results of measurements the resistance of the construction materials against acids permeation by using the modified MIKROTEST method, modified MINITEST method and the KONDUKTOTEST method

Each set of measurements for each test chemical contained:

-9 separate MIKROTEST sets;

-1 separate MINITEST set with 20 independent measuring places;

-4 permeation cells of KONDUKTOTEST device, two of them have been tempered to 30°C and two have been left at normal laboratory temperature.

Results of the statistical evaluation of the smallest sample thickness used for all three measurement methods have been calculated with PE for all test chemicals in the range of 0.105 to 0.109 mm, for PEVA in the range of 0.096 to 0.102 mm for BPM of 0.304 to 0.309 mm and for Tyvek from 0.168 to 0.181 mm. The BT values of all types of tested materials in relation to the test chemicals used by all methods are summarized in table 2. The time value corresponds to the deduced and subsequently statistically evaluated the lowest BT value. Where time is not listed, BT has not been reached within 480 min and the measurement has been terminated. The figures given in the numerator correspond to the results of the measurements carried out at 30 °C and in the denominator at normal laboratory temperature.

Only two permeations for a duration of 480 min have been registered in case of the permeation study of test chemicals through PE. Permeation of HNO, has been statistically evaluated in terms of the minimum BT value and it was 164.7 min and in the case of HCOOH was 383 min. However, the permeations of both acids have been very gradual at low gas concentrations. The measurement was ended based on a comparison of the indicator standard papers after their test for a colour reaction corresponding to the gas permeability. Figure 7a shows the surface HCOOH permeation through the tested material at the time when it was decided to finish the measurement and BT determination. After decomposition of the MINITEST set, no evidence of its destruction has been visible on the tested material sample. Measurements have shown that the PEVA tested material is resistant to all acids except for HCOOH. In this case the minimum BT value has been calculated for 228.5 min. As in the previous case, the decision to end the measurement has been associated with a difficult detectable colour change (fig. 7b).

Unlike the PEVA foil both PE foil and the BPM containing foil, there have been signs of destruction, even though the BT value has not always been found. A direct contact of H₂SO₄ with PEVA foil has caused irreversible staining of nearly clear tested material into yellow to brown colour while the test chemical has been irreversibly coloured (fig. 8a). The BPM foil has changed its structure and very intensively swelled after a long contact with HNO₂ at the

 Table 2

 RESULTS OF THE RESISTANCE MEASUREMENT OF TESTED MATERIALS AGAINST THE EFFECTS OF TESTED CHEMICALS

RESULTS OF THE RESISTANCE MEASUREMENT OF TESTED MATERIALS AGAINST THE EFFECTS OF TESTED CHEMICALS												
Tested	MIKROTEST				MINITEST				KONDUKTOTEST			
acids	PE	PEVA	BPS	Tyvek	PE	PEVA	BPS	Tyvek	PE	PEVA	BPS	Tyvek
HCl	>480	>480	>480	153.0	>480	>480	>480	260.7	>480	>480	>480	>480
H ₂ SO ₄	>480	>480	>480	>480	>480	>480	>480	>480	>480	>480	>480	>480
HNO ₃	164.7	>480	294.3	281.5	160.4	>480	293.7	279.3	>480	>480	220.5 261.5	>480
H ₃ PO ₄	>480	>480	>480	>480	>480	>480	>480	>480	>480	>480	>480	>480
CH₃COOH	>480	>480	>480	>480	>480	>480	>480	>480	>480	30 37.5	>480	>480
HCOOH	383.7	228.5	>480	228.6	382.7	299.1	>480	287.3	>480	282.5	>480	>480

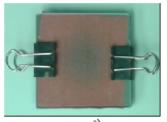




Fig. 7. Detected changes in the indication layer colour: a) the visible change of the indication layer colouring after the HCOOH permeation through PE, b) registered change of the indicator layer colour after permeation of HCOOH through PEVA





Fig. 8. Destruction effects of tested materials after prolonged exposure to acids: a) browning PEVA foil after the long contact with H₂SO₄, b) indication of irreversible destruction of material based on BPM after exposing HNO₃ at the BT

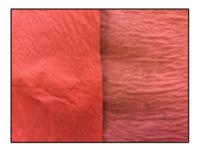


Fig. 9. Difference in the indication layer colour before (left) and after (right) measurement of PE foil for HCOOH

site of the direct contact with this acid (fig. 8b). It can reasonably be assumed that in the case of very significant permanent and irreversible swelling, it may be a damage to the internal structure of the BPM layer which is no longer capable of restoring its original properties, presumably because of the breakage of its linear polymeric chains. It was further observed that after decomposition of the MIKROTEST measuring set, the sample at the contact site has been brown, strongly swollen and BPM had a consistency like gelatine. After further exposure to HNO₃, characterized by its dangerous oxidizing and corrosive properties, the brown colour has become even more intense, indicating the possibility of carbon transition from isobutylene-isoprene rubber macromolecules into its oxidized forms.

After exposure to all acids, swelling of the PEVA tested material has been observed. Although there is a general assumption that swelling is associated with dissolution of the polymers and at the same time with the increase in the diffusion rate value and thus the permeation of the material, this theoretical consideration has been confirmed in the case of HCOOH and the PEVA tested material.

Tested material Tyvek designed to protect against the effects of organic chemical compounds is useful to provide with a long-lasting body surface protection against exposure to H₂SO₄, H₃PO₄ and CH₃COOH. In the case of HCl, the lowest BT value (153 min) has been achieved. In the case of HNO₃ 281.5 min and for HCOOH 228.6 min. Samples of Tyvek tested material did not show any noticeable changes of destruction. Even in the case of this material there were no mass acids permeations, which resulted in the difficult determination of the exact BT. The reasons for the difficult identification of BT have been the slight changes of an area character, which gradually and very slowly acquired intensive colouring.

The modified MINITEST method has been used as a direct alternative to the MIKROTEST method, varying in different layouts and other geometry of samples. A minor

disadvantage is the fact that the seal of the set has been more problematic than the individual MIKROTEST sets. Measurements made with PE foil and HCOOH need to be repeated several times because of the very difficult verification of the obtained results. Probably due to the leakage of the measuring set, it was not possible to identify the individual sampling sites as the acidic vapours spread across the indicating layer. Figure 9 shows a clear difference between the indication layer colouring before and after the measurement.

By comparing the data on the results from table 2, it is possible to get at the conclusion that has been assumed. For both colorimetric methods, the same results have been obtained from a simple comparison of the tested material against the test chemical. In practice, it means that if the real result has been measured by the modified MIKROTEST method, it was also measured by the modified MINITEST method, which means that 7 possible samples have been evaluated in the 24 possible combinations for both methods. In the case of a qualitative comparison of the results, the best matches have been achieved in the case of BPM, where the differences in the order of the units of minutes have been recorded, thus no more than 5 %. Totally different results have been obtained when comparing values in relation to HCl and HCOOH, where differences have been found in the scope from approximately 0.03 % to 58 %. Such a significant difference is not caused due to the different thickness of the used samples.

In terms of the test chemicals destructive effects evaluation, it can be stated that they have been very similar and therefore comparable between both colorimetric methods. Figure 10a shows the result after exposure to BPM film by HNO₃ and figure 10b after exposure to HCl. In the case of HNO₃, this was a process where BT has been recorded, meaning that protective properties have been totally lost, whereas in the case of HCl it did not get to

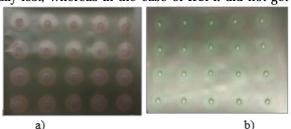


Fig. 10. Destruction of BPM material: a) after the effect of HNO₃, b) after the effect of HCl

permeation. It has been proved that discoloration of the tested material sample after the reaction of HCl with the corresponding colour component of the polymeric material does not have to lead to loss of protective properties. The disruption of the structure of polymeric material chains based on non-polar non-crosslinked elastomers will always be probably a fundamental contribution to the loss of

protective properties.

The results obtained by the KONDUKTOTEST method have shown that the results achieved by simple contact colourmetric methods cannot be compared with each other, not only in terms of the number of tested materials for which permeation has been recorded but also in terms of comparison of the resulting BT. It turns out that the method of rapid evaluation of test chemicals permeation by lag-time in those measurements that last for a long time and in which permeation occurs slowly is not appropriate and that the permeation comes earlier. Moreover, it is necessary to emphasize that a linear increase in the concentration of the test chemical in the redistilled water must be achieved. This is, however, associated with the relatively mass permeation of the test chemical through the tested barrier material. In practice, this means that before the user is able to evaluate the BT in this way, it is very likely to move at a time when permeation actually has occurred. However, this theory needs to be further verified experimentally. Many of the results identified by the KONDUKTOTEST method have been typical of the occurrence of two linear increases in concentration of the toxic substance over time. It is therefore more difficult to decide which one corresponds to the actual BT. The real solution is to extrapolate the results of measurement by MS Excell. This software allows a clear determination of the test chemical permeation and the first linear increase in the concentration of the toxic substance in the collection medium. Consequently, the use of the KONDUKTOTEST method is unlikely to be susceptible to samples whose resistance to toxic agents will be lower and to samples within those come to rapid and mass permeation of toxic substances over a short period of time. Very good results have been obtained for all used test chemicals within the carbon electrodes calibration. It is also probable that there is a problem related to a different approach to the measurement. For colorimetric methods, the sample of the test material is in direct contact with the test chemical and the detection layer, but for the KONDUKTOTEST method, the distance between the back side of the sample and the redistilled water level is approximately 1 cm. Not only the permeation through this layer of the air affects negatively the process of BT evaluation, but it is also possible to reasonably believe that measurement of the long-term permeation characteristics will lead to condensation of water on the back side of the sample in which primary vapor permeation will be absorbed without being registered with electrodes. If this condensate sticks to the walls of the measuring device and does not reach the level of redistilled water, the electrodes do not record any concentration increase. Comparison of the usability of simple contact methods working on the basis of the color change of acid-base indicators (Kongo red) with a method based on classical conductivity and using modern and standardized approaches to the evaluation of barrier materials has been done.

Conclusions

The results have unambiguously shown that simple methods did not lose their signification and are still usable. Further research will focus on changing the permeation cell design, which will be adapted to simulate more closely

the contact conditions of measurements. Both approaches to testing have confirmed their undisputed benefits and have shown some of their negatives, which will need to be further verified and discussed. It has turned out that the possibility of interpreting standardized calculations using the KONDUKTOTEST method is crucial in these types of measurements and that the BT fast reading method somewhat fails. It has also been shown that contact methods using the colourmetric principle of evaluation are very sensitive. It will be a question of further verification whether this sensitivity corresponds to or does not correspond to the first detectable change in conductivity increase. If this approach is confirmed, the applicability of both principles could still be considered in real terms.

References

1.STODOLA, P., Algorithms, 11, no. 74, 2018, p. 1.

2.***, Doctrine of the Czech Armed Forces. Vyskov, 2004, p. 147.

3.OTRISAL, P., FLORUS, S., Proceedings of the 7nd International Conference: Inhabitant Protection: Dekontam 2013, Ostrava, Vzech Republic, 2013, p. 110.

4.MOSTEANU, D., BARSAN, G., OTRISAL, P., GIURGIU, L., OANCEA, R., Rev. Chim. (Bucharest), **68**, no. 11, 2017, p. 2499.

5.HOROVA, I., KOLACEK, J., VOPATOVA, K., Comput. Statistics & Data Analysis, **57**, no. 1, 2013, p. 364.

6.POPESCU, V., SANDU, I., C.A., POPESCU, G., Rev. Chim. (Bucharest), **67**, no. 12, 2016, p. 2454.

7.STANESCU, M.D., FOGORASI, M., DOCHIA, M., MIHUTA, S., LOZINSKY, V.I., Rev. Chim. (Bucharest), **60**, no. 1, 2009, p. 59.

8.STEPANEK, B., OTRISAL, P., Croatian J. Ed., 14, no. 1, 2012, p. 169. 9.OTRISAL, P., Croatian J. Ed., 14, no. 1, 2012, p. 123.

10.OTRISAL, P., FLORUS, S., Chemicke listy, 108, no. 12, 2014, p. 1168. 11.OTRISAL, P., FLORUS, S., BARSAN, G., MOSTEANU, D., Rev. Chim. (Bucharest), **69**, no. 2, 2018, p. 300.

12.OTRISAL, P., FLORUS, S., Proceedings of the 33rd International Symposium: Industrial Toxicology 2013, Bratislava, Slovak Republic, 2013, p. 91.

13.PETREA, N., GINGHINA, R., PRETORIAN, A., PETRE, R., BARSAN G., OTRISAL, P. MOSTEANU, D., Rev. Chim. (Bucharest), **69**, no. 7, 2018, p. 1640.

14.HOSKOVA-MAYEROVA, S., MATURO, A., Italian J. Pure Appl. Math., **39**, no. 2, 2018, p. 701.

15.PARTENI, O., RADU, C.-D., MURESAN, A., SANDU, A.V., OPROIU, L.-C., CIOBANU, L., SANDU, I.G., Rev. Chim. (Bucharest), **66**, no. 11, 2015, p. 1780.

16.RADU, C.D., DANILA, A., SANDU, I., MURESAN, I.E., SANDU, I.G., BRANISTEANU, E.D., Rev. Chim. (Bucharest), **68**, no. 6, 2017, p. 1345. 17.PANAITESCU, C., JINESCU, C., MARES, A.M., Rev. Chim. (Bucharest), **67**, no. 5, 2016, p. 925.

18.KMOCHOVA, A., TICHY, A., ZARYBNICKA, L., SINKOROVA, Z., VAVROVA, J., REHACEK, V., DURISOVA, K., KUBELKOVA, K., PEJCHAL, J., KUCA, K., J. Appl. Biomed., **14**, no. 1, 2016, p. 19.

19.PRIKRYL, R., OTRISAL, P., OBSEL, V., SVORC, L., BUK, J., Nanomaterials, **8**, no. 9, 2018, p. 679.

20.SVORC, L., STREZOVA, I., KIANICKOVA, K., STANKOVIC, D., OTRISAL, P., SAMPHAO, A., J. Electroanal. Chem., 822, no. August, 2018, p. 144.

21.SCARLET, R., MANEA, L., R., SANDU, I., CRAMARIUC, B., SANDU, A., V., Rev. Chim. (Bucharest), **63**, no. 8, 2012, p. 777.

22.POPA, M., MAMALIGA, I., PETRESCU, S., TUDOSE, E., T., Rev. Chim. (Bucharest), **66**, no. 5, 2015, p. 668.

23.POPESCU, V., SANDU, I., C.A., POPESCU, G., Rev. Chim. (Bucharest), **67**, no. 10, 2016, p. 1994.

24.CIOCA, L.I., MORARU, R.I., BABUT, G.B., The 15th International Conference Knowledge Based Organization, Nicolae Balcescu Land Forces Academy, Sibiu, Romania, 2009, **2**, p. 44.

25.CIOCA, L.I., MORARU, R.I., BABUT, G.B., Proceedings of the International Conference on Risk management, assessment and mitigation, Bucharest, Romania, 2010, p. 56.

- 26. LAKATOS, E.S., CIOCA, L.I., DAN, V., CIOMOS, A.O, CRISAN, O.A, BARSAN, G., Sustainability, **10**, 2018, p. 332. doi:10.3390/su10030865 27.MOSTEANU, D., TREFAS, L., TREFAS, A.-S., MOSTEANU, R., The 21st International Conference Knowledge Based Organization, Nicolae Balcescu Land Forces Academy, Sibiu, Romania, 2015, p. 209.
- 28.GIURGIU, L., BARSAN, G., MOSTEANU, D., The 9th International Management Conference: Management and Innovation For Competitive Advantage, Bucharest, Romania, 2015, p. 506.
- 29.MOSTEANU D., HALMAGHI, E.E., 18th International Conference The Knowledge-Based Organization: Management and Military Sciences, Conference Proceedings 1, Sibiu, Romania, 2012, p. 548.
- 30.CUC, S., BUNGAU C., Management between profit and social responsibility, Review of Management and Economic Engineering International Management Conference, Cluj Napoca, Romania, 2014, p. 186.
- 31.CUC, S., TRIPA, S., BUNGAU, C., 5th Review of Management and Economic Engineering International Management Conference, Cluj Napoca, Romania, 2016, p. 100-+.
- 32.VLAD, D., CIOCA, L.I., 10th International Conference Interdisciplinarity in Engineering, INTER-ENG 2016, Procedia Engineering, Tirgu Mures, Romania, 181, 2017, p. 324.
- 33.VLAD, D., CIOCA, L.I., 9th International Conference Interdisciplinarity in Engineering, INTER-ENG 2015, Procedia Technology, Tirgu Mures, Romania, **22**, 2016, p. 60.
- 34.FLORUS, S., OTRISAL, P., Chemicke listy, 108, no. 9, 2014, p. 838. 35.OTRISAL, P., OBSEL, V., BUK, J., SVORC, L., Nanomaterials, **8**, no. 8, 2018, p. 564.
- 36.POPESCU, V., PUI, A., SANDU, I.C.A., POPESCU, G., Rev. Chim. (Bucharest), **67**, no. 2, 2016, p. 270.

- 37.BUNGAU, C., GHERGHEA, I.C., PRICHICI, M., Conference: 1st Management Conference on 20 Years After: How Management Theory Works, Book Series: Review of Management and Economic Engineering International Management Conference, Cluj-Napoca, Romania, 2010, p. 188.
- 38.SVORC, ¼., HASSO, M., SARAKHMAN, O., KIANICKOVA, K., STANKOVIC, M., D., OTRISAL, P., Microchem. J., **142**, no. November, 2018, p. 297.
- 39.TULBURE, E.A., SANDU, I.G., ATODIRESEI, G.V., SANDU, I., Rev. Chim. (Bucharest), **64**, no. 7, 2013, p. 736.
- 40.BUNGAU, C., BLAGA, F., GHERGHEA, C., Conference: 2nd Review of Management and Economic Engineering Management, Proceeding: Management of Crisis or Crisis of Management?, Book Series: Review of Management and Economic Engineering International Management Conference, Cluj Napoca, Romania, 2011, p. 36.
- 41.CSOKMAI, L.S., TARCA, R.C., BUNGAU, C., HUSI, G., Int. J. Comput. Commun. Control, 10, no. 1, 2015, p. 30.
- 42.***, A pure chemicals and particularly pure substances. Chemical indicators. Preparation of indicator solutions. Prague: The Office for Standardization and Measurement, 1980.
- 43.OBSEL, V., OTRISAL, P., FLORUS, S., Proceedings of the 2nd Conference: Hazmat Protect, Milin, Czech Republic, 2016, p. 166. 44.OBSEL, V., OTRISAL, P., FLORUS, S., Methodology Konduktotest, Vyskov, Czech Republic, 2016, 20 p.
- 45.OTRISAL, P., FLORUS, S., SVORC, L., BARSAN, G., MOSTEANU, D., Mat. Plast., **54**, no. 4, 2017, p. 748.

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