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PROPOSAL FOR A METHOD FOR TESTING RESISTANCE OF CLOTHING AND GLOVES TO PENETRATION BY PESTICIDES

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Abstract: The paper presents the proposal for a method for testing the resistance of materials used for the production of protective clothing and gloves to penetration by concentrated chemical preparations of pesticides. It has been based to a large extent on the recommendations of European standards, with certain modifications resulting from the specific properties of non-volatile and non-water-soluble biologically-active components of pesticides. These modifications primarily involved the use of a solid sorption medium and adjustment of research apparatus to the research conditions consistent with the proposed method. The results of preliminary studies on penetration of the selected biologically-active components of pesticides (dichlorvos, 2,4-D, cypermethrin, carbofuran) through the selected protective materials (fabric coated with viton and butyl on both sides, rubberised fabric, butyl rubber) are presented. The study confirmed the usefulness of the proposed method for testing the resistance of materials protecting against the effect of pesticides.

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INTRODUCTION

The use of crop protection agents, appart from undoubted benefits, is associated with serious risk for the health of workers exposed to their activity. Therefore, it is necessary to equip the workers with appropriate personal protection equipment, among which protective clothing and gloves play an important role. Besides the respiratory and gastrointestinal tracts, intact skin is another important route for the absorption of crop protection agents. Numerous studies carried out by various research centres indicate that the skin is exposed to considerably higher doses of chemicals than other parts of the human organism [13]. In some cases, the potential dermal exposure may reach such high proportions as 94.2–99.8% of total exposure. Thus, it becomes clear that using protective clothing and gloves providing the required level of protection is essential to reduce the exposure of workers to the activity of crop protection agents.

Because of varied chemical composition, specific properties and considerable toxicity of the preparations used in agriculture, the requirements concerning clothing and gloves protecting workers from their activity are very strict. They concern, among others, the appropriate construction of protective equipment, their resistance to mechanical factors and - which is a prerequisite for qualification of these means as suitable for use in agriculture - resistance to penetration by crop protection agents. Neither European nor Polish Standards concerning the determination of resistance of protective materials to the activity of pesticides have been developed to date. Taking into consideration the importance of this issue, work is in progress aimed at adjust the chromatographic method used in the Central Institute for Labour Protection

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to determine highly volatile substances for use in the examination of barrier materials from which clothing and gloves protecting against liquid pesticides are made. The modified method has been based to a large extent on the method of testing the resistance of clothing and gloves to penetration by liquid chemicals, recommended by European Standards [2, 3]. However, because of the specific character of crop protection agents, it was necessary to introduce certain changes in the method. The modifications described in the paper involve primarily the use of a different sorption medium for pesticides penetrating through the tested material in liquid form. This resulted from the fact that for non-volatile biologically-active substances constituting the main components of crop protection agents, the gas or liquid sorption medium could not be applied. For the above reasons, the search for a solid sorption medium possessing appropriate parameters was initiated. On the basis of preliminary tests it was established that pneumothermic polypropylene non-woven is characterised by good sorptive properties and can be used to absorb pesticides [8]. The consequence of the change of type of sorption medium was the necessity to modify the construction of elements of the test stand - the so-called penetration cells, in which the process of penetration of the preparation through clothing material and gloves takes place. The tests, utilising a solid sorption medium, imposed the periodic character of the whole method. Therefore, the determination of protective parameters of the tested materials was possible not on the continuous basis as in the on-line system used previously, but on certain measurement points in the course of the whole test. Using the periodic method was much more difficult and time-consuming, in particular with respect to the extraction of biologically-active ingredients from the non-woven and preparation of samples for analysis by gas chromatography method.

In the course of development of research methodology it was established that the resistance of materials for permeation by specific biologicaly-active substances, and not their imitators, should be determined. For this purpose - taking into consideration the physico-chemical properties, usable forms and common use, as well as the toxicity and absorption routes of crop protection agents - a selection was carried out which allowed the assembly of an optimum set of four model biologically-active substances, namely: dichlorvos, cypermethrin, carbofuran, 2,4-D [7].

MATERIALS

Test samples. The tests were carried out on the following coated fabrics used for production of protective clothing and gloves:

- Rubberised fabric of 0.42 mm thickness and surface mass of 471 g/m^2 (protective clothing);
- Fabric coated on both sides with viton and butyl of 0.43 mm thickness and surface mass of 607 g/m^2 (protective clothing);
- Butyl rubber of 0.60 mm thickness and surface mass of 701 g/m^2 (5-digit hermetic protective gloves).

Sorption material. Pneumothermic polypropylene non-woven (melt blown) of 40 g/m^2 surface mass and 4.2 µm, mean fibre diameter was used for sorption of biologically-active ingredients permeating through the tested protective materials.

Reagents. The tests were carried out using commercially available concentrated crop protection agent preparations:

- WINYLOFOS 550 EC (toxicity class II) with 550 g/l dichlorvos concentration, produced by the Chemical Plant "Organika –Azot" SA, Jaworzno, Poland;
- CYPERKILL 25 EC (toxicity class III) with 25% concentration of cypermethrin (Mitchell Cotts Chemical Ltd., UK);
- Seed dressing agent Furadan 480 FS (toxicity class I) with 480 g/l carbofuran concentration (FMC Corporation, USA);
- AMINOPIELIK 720 SL (toxicity class III) with 720 g/l 2,4-D concentration (Chemical Plant "Rokita" SA, Brzeg Dolny, Poland).

Solvents. The following solvents were used for extraction of active ingredients absorbed by the sorption non-woven:

- Acetone in the case of dichlorvos and cypermethrin extraction;
- Diethyl ether in the case of carbofuran extraction;
- Distilled water in the case of 2,4-D extraction.

METHODS

Apparatus. The resistance of protective materials to penetration by concentrated crop protection agents was tested by means of apparatus consisting of:

- Permeation test cell for testing clothing material;
- Permeation test cell for testing glove material;
- Laboratora 400 vacuum evaporator (Heidolph) with water bath;
- Ati Unicam 610 gas chromatograph.

For testing of protective clothing and gloves, two different penetration cells of different dimensions and construction were used. This difference resulted from the recommendations of two relevant European Standards [2, 4], reflecting most accurately the actual conditions under which the particular elements of protective clothing are used, and were therefore followed in our methodology. The differences concerned primarily the following:

- **Different positioning of the examined fabric sample.** For testing glove materials, a two-chamber penetration cell was used in which the tested chemical compound was separated from the sorption medium by the test material sample, positioned vertically according to the EN 374-3 standard (Fig. 1), whereas the penetration cell used for testing clothing materials was characterised by horizontal

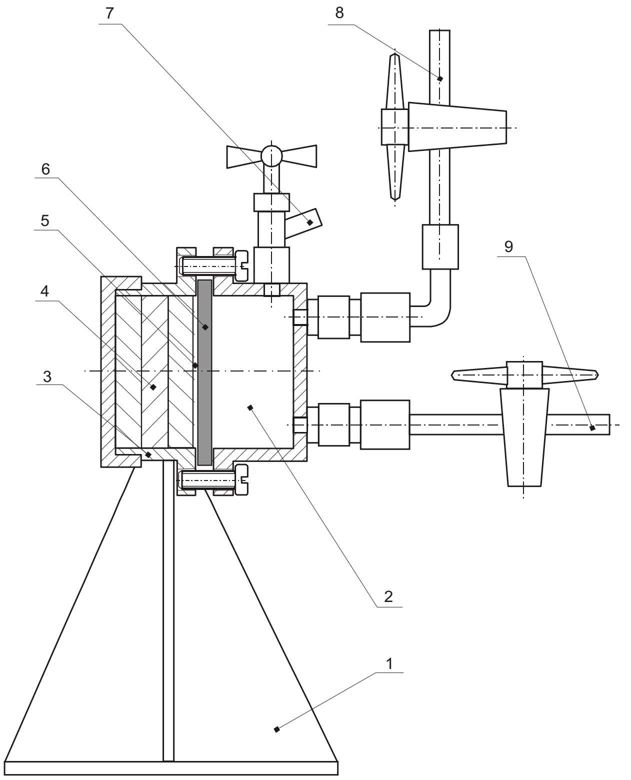

Figure 1. Construction of the permeation test cell used for testing resistance of glove materials to penetration by concentrated crop protection agents. Components: 1. stand, 2. chamber with agent, 3. chamber with sorption non-woven, 4. metal rings used to fill the interior of chamber, 5. sorption non-woven, 6. test material sample, 7. venting valve, 8. inlet pipe, 9. outlet pipe.

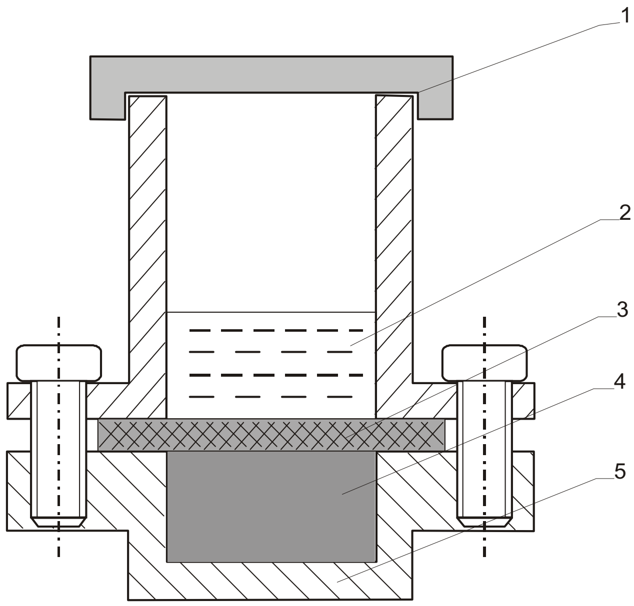

Figure 2. Construction of the permeation test cell used for testing resistance of clothing materials to penetration by concentrated crop protection agents. Components: 1. Loose cover, 2. chamber with agent, 3. test material sample, 4. sorption non-woven, 5. chamber with sorption non-woven.

positioning of the material sample according to the EN 369 standard (Fig. 2).

• **Diameter of the samples exposed to direct effect of crop protection agents.** In the case of tests carried out on clothing materials, the diameter of the tested samples was 30 mm and was twice as small as the glove material samples, which were 60 mm in diameter. The differences in test sample dimensions result from different dimensions of the penetration cells used for testing clothing and gloves.

• **Volumes of crop protection agents used for testing.** Because of the different capacity of the equipment, the penetration cell used for testing clothing materials was filled with 10 ml of concentrated crop protection agent, whereas the analyses utilising the cell for glove testing required almost a five times larger volume of the preparation (45 ml).

Both cells were suitable for tests conducted on a continuous basis using a gas sorption medium, and their construction was initially completely consistent with the descriptions given in the EN 374-3 and EN 369 standards. On the basis of preliminary test results it was established that because of the low volatility of biologically-active substances it was impossible to analyse the quantity of substances penetrating through the materials in continuous testing system. Thus, it was necessary to conduct the tests using a periodic system and an appropriately selected solid sorption medium. This was associated with the necessity to modify the penetration cells so that a solid sorption medium could be used. The modification concerned only one chamber of the cell - the lower one in the apparatus used for testing clothing material and one of the lateral chambers of the cell used for testing gloves. It involved the removal of pipes supplying gas medium to the cell. In this way, containers were obtained allowing the placing of sorption non-woven inside and its easy changing during the tests without losing the tightness of the sample preparation system. The dimensions of the modified chambers were additionally regulated by using metal rings of a diameter equal to the internal diameter of the chamber and of different heights.

For evaporating the extracts of active ingredients obtained by washing the sorption non-woven with solvents the vacuum evaporator was used.

Quantitative determination of the selected substances permeating the tested material samples was conducted using the gas chromatograph, equipped with an electron capture detector and a set of packed columns with appropriate distributive properties. The determination of the selected active ingredients was carried out using the following types of columns [1, 6, 9-12]:

• For dichlorvos: packed column of 2.5 m length and 3 mm diameter, packing 10% DC-200 + 15% QF-1 with support Chromosorb, mesch 80/100;

• For cypermethrin: packed column of 1.5 m length and 3 mm diameter, packing 6% OV 101 with support Diatomit C'Q', mesch 80/100;

• For 2,4-D: packed column of 1.5 m length and 4 mm diameter, packing 3% SE-30 with support Chromosorb WHP, mesch 80/100;

• For carbofuran: HP-5 capillary column of 10 m length and 0.53 mm diameter, packing cross-linked phenylsilicone resin (5%), film thickness 2.65 µm.

Testing procedure. The tested material sample was positioned between the two chambers of the permeation test cell so that its external surface (right side) was in contact with the crop protection agent preparation, whereas the internal (rear side) was in direct contact with the sorption non-woven. Then, the preparation of the tested crop protection agent was poured into the chamber through the inlet in an amount corresponding to the chamber capacity (10 ml in the case of clothing materials; 45 ml for gloves) and the testing time recorded from that moment. The tests were conducted by the so-called periodic system, at certain time intervals (10, 30, 60, 120, 240 and 480 minutes from the beginning of the test) consistent with the protective classes defined in the EN 466 and EN 374-1 standards; then the sorption non-woven was collected for analysis, and a new one was inserted in its place. This technique did not allow for continuous monitoring of the penetration process, but it was necessary because of the type of sorption medium used. The contact of the tested material samples with pesticides took place in the penetration cell. The samples were positioned so that their external surface (right side) was in contact with the crop protection agent, whereas at the rear side nonwoven sorption material rings were placed, which, after the aforementioned time intervals, were collected for analysing the absorbed quantities of biologically-active substances. In order to extract the active ingredient, the non-woven was placed in a flask with a tightly fitted stopper, in which the extraction process was conducted. Extraction, depending on the analysed substance, was carried out:

• in a single stage (for 2,4-D with distilled water - 10 ml),

• in two stages (for cypermethrin and dichlorvos with acetone - 10+10 ml),

• in three stages (for carbofuran with diethyl ether - 10+5+5 ml),

using the same solvent for all the stages. The obtained extracts were condensed by evaporating under vacuum conditions to either dry residue (in the case of determinations carried out for carbofuran and 2,4-D) or to minimum volume of 2–3 ml (in the case of cypermethrin and dichlorvos). Dry residues and condensed extracts were then dissolved in appropriate solvents (acetone in the case of cypermethrin dichlorvos, and of carbofuran, and n-hexane in the case of 2,4-D analysis) to obtain 10 ml volumes.

Table 1. Classification of protective materials according to resistance classes.

Class	Breakthrough time
6	>480
5	>240
4	>120
3	>60
2	>30
1	>10

From the obtained volume of the extract, the following amounts were injected with a microsyringe onto the gas chromatograph column:

• 10 µl of dichlorvos or cypermethrin extract,

• 1 µl of carbofuran or 2,4-D extract.

Chromatographic determinations were carried out three times. The detectability of the active ingredients, defined as the smallest mass that could be determined, amounted to:

• 0.10 µg carbofuran or dichlorvos on sorption non-woven filter,

• 0.05 µg cypermethrin or 2,4-D on sorption non-woven filter.

Figure 3 presents schematically the testing procedure.

As a result of the tests, chromatograms were obtained from which the surface areas of the peaks were read, and then, using standardisation curves, the concentrations of active ingredients in the analysed extracts were determined. Having known the concentration of ingredients, the permeation rate of the particular substance through the tested material was calculated for the particular time intervals (10, 30, 60, 120, 240 min) using the following formula [2]:

$$P = \frac{C_x \times W}{n(T_i - T_{i-1}) \times A} \quad [\mu g/cm^2 \ min] \qquad (1)$$

where:

P - permeation rate [µg/cm^2 min];

A - sample area (4.9 cm^2 for clothing material, 20.4 cm^2 for gloves material);

i - index number assigned to each measurement (for the first measurement - i = 1);

T_i - collection time of the *i* sample of sorption non-woven [min];

C_x - concentration of the active ingredient read from the calibration curve [µg/ml];

W - coefficient proportional to the order of dilution of the extract;

$\bar{n}$ - mean recovery coefficient of the active ingredient from sorption non-woven.

Taking into consideration the permeation rate, the protective parameter - breakthrough time - was determined, defined according to the EN 369 and EN 374 standards as the time interval elapsing from the moment

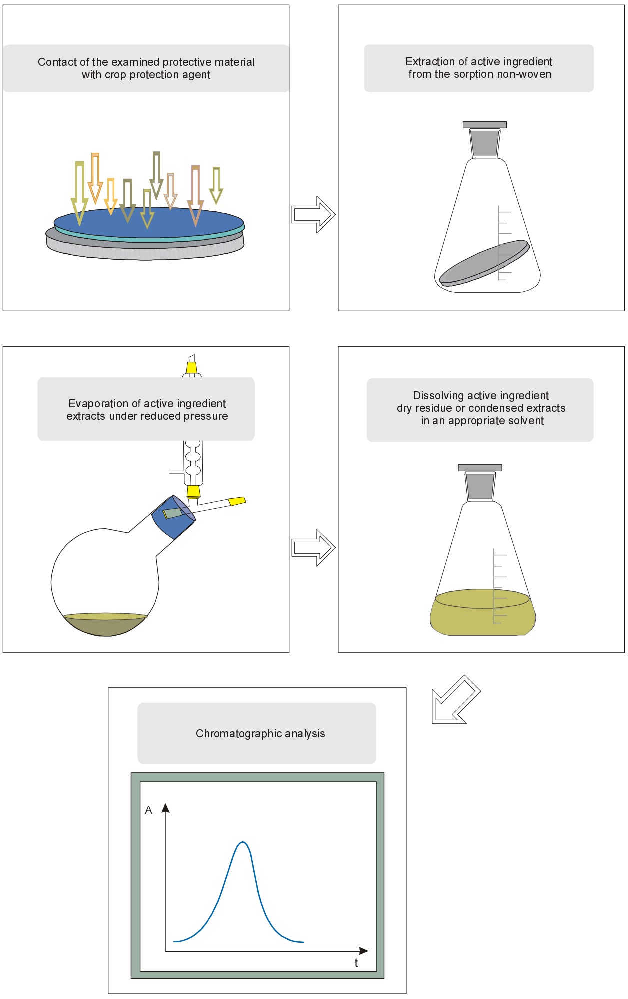

Figure 3. Scheme of the testing procedure.

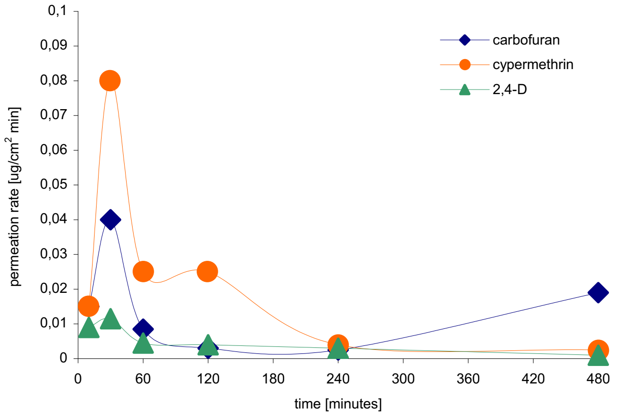

Figure 4. **C**hanges of permeation rates of carbofuran through fabric coated on both sides with vitone and butyl, and cypermethrin and 2,4-D through butyl rubber (mean for two samples).

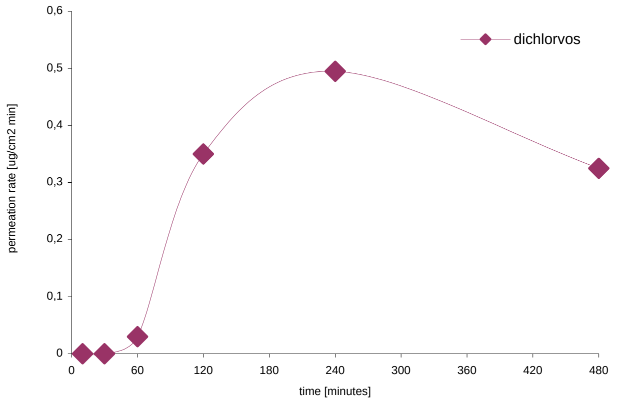

Figure 5. Changes of permeation rate of dichlorvos through rubberised fabric (mean for two samples).

of contact of the chemical substance with the top side of the tested material until the permeation rate of the substance reaches the value of 1 µg/cm^2 min. The “breakthrough time” value defines the time of safe use of protective clothing and gloves made of the tested materials under conditions involving exposure to toxic chemicals.

The division of protective materials with respect to the classes of resistance to penetration by chemical substances are presented in Table 1 [3, 5].

Number of tests. Altogether, two samples of fabric coated on both sides with viton and butyl were tested for penetration by carbofuran, and two samples of rubberised fabric were tested for penetration by dichlorvos. Two samples each of butyl rubber were tested for penetration by cypermethrin and 2,4-D.

RESULTS

Protective clothing materials were tested for penetration by two active ingredients - dichlorvos and carbofuran. The other two substances - cypermethrin and 2,4-D were tested on samples collected from gloves. During the tests, the permeation rates of particular ingredients through the tested protective materials were analysed. Figures 4 and 5 present the changes of permeation rate during 8 h (480 min) testing time. In order to increase the legibility, the data obtained from measurements have been presented in the form of two diagrams (Figures 4 and 5).

Comparing the permeation rate values of all four substances obtained for different time points with the threshold value (1 µg/min cm^2) it was established that this was never exceeded. This means that the tested materials are characterised by at least 8-hour resistance to the active ingredients of crop protection agents and they may be classified as belonging to the highest - sixth class of resistance. The obtained breakthrough time values exceeded in all cases the value of 480.

DISCUSSION

The aim of the study was to establish whether the proposed method could be used to determine the resistance of protective clothing materials to penetration by concentrated crop protection agents. The tests indicated the usefulness of the method for determinations of this type, and confirmed the appropriateness of the introduced modifications. The specific properties of crop protection agents required utilisation of a solid sorption medium, which necessitated the application of periodic method of testing characterised by a limited possibility of continuous monitoring of the process of substance penetration through the tested material in comparison with the continuous method. However, this modification did not lead to incorrect interpretation of results and difficulty in classification of the tested materials to particular protection level groups, because this classification was taken into account at the time of samples collection for analysis.

The protective clothing materials selected for testing demonstrated high resistance to penetration by concentrated crop protection agents. On the basis of the obtained results, it was established that the determined breakthrough time of the fabric coated on both sides by viton and butyl by carbofuran, and of the rubberised fabric by dichlorvos, as well as that of butyl rubber by cypermethrin and 2,4-D, exceeded 480 minutes. This means that these materials can be classified as belonging to the group of materials characterised by the highest resistance - class 6. Thus, it is recommended that is made of individual protective clothing made of these materials during work in agriculture, which involve contact with crop protecting agents containing the tested active substances as the main components.

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