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Selection of Sorption Material for Tests of Pesticide Permeation Through Protective Clothing Fabrics

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The paper presents the results of studies on selecting a solid sorption material for absorbing liquid crop protection agents which permeate samples of protective clothing fabrics. The sorption materials were investigated and selected with an assumption that they should have a high recovery coefficient for biologically active substances, used as active ingredients in crop protection agents, at a presumed, acceptably high level. The selected substances were determined with a gas chromatograph equipped with an electron capture detector (dichlorvos, cypermethrin and 2,4-D) and a nitrogen-phosphorus detector (carbofuran).

The tests demonstrated that polypropylene melt-blown type unwoven cloth had high recovery coefficients for all 4 active ingredients proposed for the study. The highest recovery coefficient, –.97, was obtained for carbofuran. The recovery coefficients obtained for the 3 remaining substances were lower: .89 for cypermethrin and 2,4-D, and .84 for dichlorvos.

pesticides active ingredients dichlorvos cypermethrin 2,4-D, carbofuran determination gas chromatography sorption sorption materials

1. INTRODUCTION

Whereas undoubtedly useful in agriculture, chemical crop protection agents are associated with serious risks for the health of the workers who are exposed to them. Therefore, it is necessary to equip workers with appropriate personal protective equipment with the right protective and functional properties. Such properties should be confirmed with complex tests of, for example, resistance to the penetration of chemicals (pesticides, in this case) and mechanical and biophysical factors. Assessment of those properties involves determining the values of parameters and comparing them with the requirements specified in standards on which assessment criteria for such protective gear are based.

In recent years, studies aimed at developing a test method and requirements for clothing protecting against liquid pesticides were undertaken by the Department of Protective Personal Equipment of the Central Institute for Labour Protection – National Research Institute. The studies concerned primarily testing the chemical resistance of coated fabric and unwoven cloth to permeation by those dangerous, toxic compounds [1, 2].

Research methodology was developed on the basis of an assumption that (a) test methods should simulate, to as great degree as possible, the actual effect of pesticides on protective clothing and (b) resistance of clothing materials to permeation should be determined with specific biologically active substances, constituting the

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active ingredients of pesticides rather than with their imitators. Literature data indicate that imitators cannot reflect the specific properties of pesticides.

Therefore, special emphasis was put on analysing workers' handling of pesticides, on the concentration of the active ingredient when workers prepare and use solutions, and on the intensity of exposure to the pesticide (aerosol, stream of liquid). The analysis showed that workers were primarily exposed to concentrated pesticides when they portioned them and prepared working solutions, whereas they were exposed to diluted pesticides while spraying the plants with crop protection agents.

Taking into consideration hazards associated with the use of liquid pesticides, it was assumed that the study should be oriented towards determining resistance of clothing fabrics to permeation by concentrated pesticide preparations and aerosols of pesticide working solutions [3, 4, 5, 6].

The starting point for the development of a methodology for determining resistance of clothing fabrics to permeation by concentrated pesticides (active ingredient content range of 30–50%) was a method of determining fabric resistance to permeation by highly volatile chemicals, specified in the PN-EN 369:1996 standard [7]. During the tests, a specific parameter, breakthrough time—defined as the time interval from the moment of the application of the substance onto the external surface of the material until the moment of its appearance in a specific quantity on the internal surface—was determined [7]. These tests were carried out in a specially designed permeation cell, which consisted of two chambers. The chemical substance was poured into the upper chamber, while a stream of air acting as a sorption medium, collecting diffused molecules of the substance and taking them to the analyser flowed through the lower one.

Because of the low volatility of biologically active substances used as active ingredients of pesticides, it was necessary to change the type of sorption medium from gas (used in testing the resistance of protective materials to permeation by, e.g., organic solvents) to a solid one. Consequently, it was necessary to modify the design of the cell specified in the PN-EN 369:1996 standard [7]. In connection with that, it was decided that tests would be carried out using a periodic method and an appropriately selected solid sorption material, which would collect the molecules of active ingredients penetrating through protective clothing material during simulated exposure to pesticides.

An analogous situation took place during the development of a methodology for testing resistance of protective clothing materials to permeation by aerosols of pesticide working solutions. The tests involved spraying a specific volume of diluted working solutions of pesticides (active ingredient content range of 1–2%) with a given velocity and under given pressure in an isolated cylinder. The aim of the test was to determine the permeation rate of the biologically active substance, defined as the ratio of the active ingredient mass which had permeated through the tested material sample to the active ingredient mass applied onto the tested material sample by spraying [8]. Also in that case, because of the low volatility of pesticides, it was necessary to use a solid sorption material.

Therefore, performing the tests first required selecting a sorption material that (a) could absorb the active ingredient molecules permeating through the tested material sample during its contact with pesticides and (b) made it possible to recover the absorbed substances by extraction with an appropriate solvent.

The paper describes studies which aimed at selecting an appropriate sorption material and determining a recovery coefficient, defined as the ratio of the quantity of the active ingredient absorbed by the sorption material to the quantity of the active ingredient which can be extracted from it. The value of this coefficient should be taken into consideration in calculating the mass of the active ingredient that penetrates the protective material and is then absorbed by the

sorption material placed in close vicinity. The selection of the sorption material was determined by the value of the obtained recovery coefficient. The more closely it approximated 1, the better recovery parameters characterised that particular sorption material.

Investigations of the recovery coefficient were preceded by a selection of a set of four model active ingredients for the study: dichlorvos (a phosphoric acid derivative), cypermethrin (a synthetic pyretroid), 2,4-D (a phenoxyacetic acid derivative) and carbofuran (a carbaminic acid derivative) [1, 2, 9]. On selection of active ingredients, their physicochemical properties, usable forms and frequency of use, as well as toxicity and absorption routes, were taken into consideration.

2. EXPERIMENTAL

2.1. Reagents and Standards

The following standards of active ingredients were used in the study: dichlorvos, cypermethrin and 2,4-D manufactured by the Institute of Organic Industry (Warsaw, Poland) as well as the standard of carbofuran manufactured by Dr Ehrenstorfer GmbH (Germany). The standards of the aforementioned active ingredients were diluted with appropriately selected solvents such as acetone (for cypermethrin, dichlorvos and carbofuran) and ethanol (for 2,4-D).

To prepare the solutions applied onto sorption material samples, solutions of the active ingredients and solvents were used. The concentrations of the active ingredients in these solutions were 0.1 mg/ml for dichlorvos and cypermethrin, and 1 mg/ml for 2,4-D and carbofuran.

To prepare standard solutions for a gas chromatograph calibration curve, the same active ingredients standards and solvents were used. Taking into consideration the linearity intervals of the instrument for the individual active ingredients, the following concentration ranges were proposed: 1.0–10.0 μg/ml for dichlorvos, 0.025–0.25 μg/ml for cypermethrin, 0.2–1.2 μg/ml for 2,4-D and 2.0–20.0 μg/ml for carbofuran. Additionally, the following reagents were used in the process of extraction: diethyl ether, n-hexane, sulphuric acid and anhydrous sodium sulphate.

2.2. Sorption Materials

To investigate the recovery coefficient for active ingredients, the following sorption materials were used:

- polypropylene melt-blown type unwoven cloth of surface mass 40 g/m^2,
- polypropylene welding needled type unwoven cloth of surface mass 112 g/m^2,
- filter fabric FPP-15 of surface mass 37 g/m^2,
- quality filter paper No. 390 of surface mass 38 g/m^2.

The diameter of the samples was 60 mm.

2.3. Apparatus

Liquid solutions of the active ingredients in appropriate solvents were applied using a graduated pipette (in the case of dichlorvos) and a microsyringe (in the case of the other substances). The solutions were applied in the form of small drops. The tip of the pipette or microsyringe needle was oriented so as to apply the drops onto the central part of the sorption material, which was placed in a glass flask. After a given volume of the solution was applied onto the filter, the flask was closed with a glass stopper.

To evaporate the extracts collected by washing the sorption material with an appropriate solvent, a rotary vacuum evaporator equipped with a water bath was used.

In view of the fact that the selected active ingredients belonged to various chemical groups of crop protection agents, it was necessary to develop individual methods of analysis.

Chromatographic analyses of the selected substances were carried out using a gas chromatograph equipped with an electron

capture detector (^{63}Ni) (to determine dichlorvos, cypermethrin and 2,4-D) and a nitrogen-phosphorus detector (to determine carbofuran) [10, 11, 12].

Because of the different physicochemical properties of the active ingredients, each of them was analysed using a chromatographic column with different distributive properties. Thus, the determination of the selected biologically active substances was carried out using the following types of columns:

- for dichlorvos: a packed column of 2.5 m length and 3 mm diameter, packing 10% DC-200 + 15% QF-1 with support Chromosorb mesh 80/100 (Vulcan, USA),
- for cypermethrin: a packed column of 1.5 m length and 3 mm diameter, packing 6% OV 101 with support Diatomite CQ mesh 80/100 (Vulcan, USA),
- for carbofuran: an HP-5 capillary column of 10 m length and 0.53 mm diameter, packing cross-linked phenylsilicone resin (5%), film thickness 2.65 μm (Hewlett Packard, USA),
- for 2,4-D: a packed column of 1.5 m length and 4 mm diameter, packing 3% SE-30 with support Chromosorb WHP mesh 80/100 (Vulcan, USA).

The following analysis conditions were used for the individual biologically active substances:

- dichlorvos: temperature of the column and the injector 147 ºC, of the detector 200 ºC, flow rate of argon 35 ml/min,
- cypermethrin: temperature of the column 255 ºC, of the injector 260 ºC, of the detector 280 ºC, flow rate of argon 55 ml/min,
- carbofuran: temperature of the column 175 ºC, of the injector 200 ºC, of the detector 210 ºC, flow rate of nitrogen 10 ml/min, of hydrogen 3.5 ml/min, of air 100 ml/min, flow rate of make-up gas 19 ml/min,
- 2,4-D: temperature of the column and the injector 200 ºC, of the detector 250 ºC, flow rate argon 45 ml/min.

Retention time of the active ingredients under the specified conditions was 25.4 min for dichlorvos, 10.6 min for cypermethrin, 2.3 min for 2,4-D, 3.6 min for carbofuran.

2.3.1. Checking the investigation equipment

Calibrating measurement equipment involved checking the linearity of indications of the gas chromatograph detector. This was checked with the standard method using an external standard. For this purpose, the prepared working standard solutions were introduced into the column of the chromatograph. Identical volumes of the solutions were injected at least in triplicate. In the case of determining dichlorvos and cypermethrin, the injected volume was 10 μl, whereas for 2,4-D and carbofuran it was 1 μl. Then, readings of peak areas were taken and an arithmetic mean was calculated. A standard curve was drawn by plotting the concentration of the active ingredient in working standard solutions on the *x* axis, and peak areas on the *y* axis. The obtained values were approximated to a straight line by the least square method. Table 1 presents the equations describing the obtained calibration curves.

2.3.1.1. Accuracy of the method. When determining the accuracy of the method, special attention was paid to checking the reproducibility

TABLE 1. Calibration Curve Equations Depending on the Determined Active Ingredients

Active Ingredient	Equation[1]	No. of Data Points	*SE*
dichlorvos	$y = 131.8\,x + 51.7$	6	43.0
cypermethrin	$y = 11906.7\,x + 14.1$	6	72.7
2,4-D	$y = 102.7\,x + 3.1$	7	4.7
carbofuran	$y = 14.4\,x + 8.6$	6	2.4

Notes. 1—in these equations *x* is expressed in μg/ml.

of the results obtained in the course of chromatographic analysis. For this purpose, several solutions of the same concentration were prepared for each active ingredient. Then the readings were checked for differences between the peak areas obtained for individual solutions. Table 2 presents the results.

Then the values of random errors were determined for the obtained results. In particular, the analysis concerned the values of the relative random error of the mean value, on the basis of which the accuracy of the method was assessed. The accuracy of measurements was defined on the basis of the relative random error of the mean value $U'_{\bar{A}}$ (at $P = .95$) [13].

Table 3 presents the calculated values of random errors and kinds of accuracy.

2.3.1.2. Detectability. The detectability of the active ingredients on sorption material samples, defined as the smallest mass that could be determined, was 0.10 μg of dichlorvos, 0.05 μg of cypermethrin, 0.05 μg of 2,4-D and 0.10 μg of carbofuran.

3. SELECTION OF SORPTION MATERIAL

During the selection of sorption material, tests were carried out. Their aim was to determine the recovery coefficients for selected active ingredients permeating through protective clothing fabric during simulated exposure to pesticides and absorbed by the sorption material placed directly under the protective fabric.

The investigations of the recovery coefficients were carried out separately for each selected active ingredient.

3.1. Investigation of the Recovery Coefficient for Dichlorvos

At the initial stage of the study, the following sorption materials were tested: polypropylene melt-blown type unwoven cloth and polypropylene welding needled type unwoven cloth. Acetone was used to extract the active ingredient from those sorption material samples.

Dichlorvos solution of 0.1 mg/ml concentration in acetone was applied onto the prepared sorption material samples placed in 0.4-, 0.6- and 1.0-ml flasks. The solution was applied in the form of

TABLE 2. Values of Peak Area Variation Coefficients for Solutions With Given Concentrations of Active Ingredients

Active Ingredient	Concentration of Solution (μg/ml)	No. of Solutions	Mean Peak Area	*SD*	*CV* (%)
dichlorvos	6.0	4	837.5 V·min	37.9	4.5
cypermethrin	0.1	2	2989.6 mV·min	110.7	3.7
2,4-D	0.4	3	40.8 V·min	1.5	3.6
carbofuran	5.0	6	65.9 V·min	3.2	4.9

Notes. *CV*—coefficient of variation.

TABLE 3. Random Error Values and Accuracy of Measurements

Active Ingredient	Concentration of Solution (μg/ml)	Relative Random Error of Mean Value $U'_{\bar{A}}$ (%)	Random Error of *SD* U_{SD}	Random Error of *CV* U_{CV} (%)	Accuracy of Measurements
dichlorvos	6.0	2.9	17.0 V·min	2.0	good
cypermethrin	0.1	3.9	82.1 mV·min	2.7	good
2,4-D	0.4	9.1	2.6 V·min	6.3	good
carbofuran	5.0	2.4	1.1 V·min	1.7	good

Notes. *CV*—coefficient of variation.

small drops. After 10 min, sorption material samples were flooded with 10 ml of acetone, and then placed on a shaker and extracted for the next 20 min. After that time, the unwoven cloth samples were taken out, placed in a beaker and washed with 2–3 acetone portions. The volume of the collected extract did not exceed 20 ml. The extract was concentrated in a vacuum evaporator at 50 ºC to the volume of 3–4 ml. Investigations of the recovery coefficient were carried out for the extract on the day of extraction and after storage until the next day. The concentrated extract was transferred quantitatively to a 10-ml measuring flask and acetone was added up to the mark. The content of dichlorvos in the extract was determined by gas chromatography.

3.2. Investigation of the Recovery Coefficient for Cypemethrin

Investigations of the cypermethrin recovery coefficient were commenced with tests utilizing polypropylene melt-blown type unwoven cloth as a sorption material and acetone as a solvent for extraction.

Cypermethrin 0.1-mg/ml solution in acetone was applied onto sorption material samples with 10- and 15-µl microsyringes. After 10 min, sorption material samples were flooded with 10 ml of acetone, and then placed on a shaker and extracted for the next 20 min. After that time, the unwoven cloth samples were taken out, placed in a beaker and washed with 2–3 acetone portions. The volume of the collected extract did not exceed 20 ml. The extract was concentrated in a vacuum evaporator at 50 ºC to solid residue and left until the next day. The concentrated extract was transferred quantitatively to a 10-ml measuring flask and acetone was added up to the mark. The content of cypermethrin in the extract was determined by gas chromatography.

3.3. Investigation of the Recovery Coefficient for 2,4-D

Investigations of the 2,4-D recovery coefficient were carried out using polypropylene melt-blown type unwoven cloth as a sorption material.

2,4-D 1-mg/ml solution was applied onto prepared sorption material samples with 40-, 70- and 100-µl microsyringes. Flasks containing the samples were left at room temperature until the next day. 10 ml of distilled water was added to each flask and left for 0.5 hr, shaken every few minutes. From each flask, 1 ml of the extract was collected and evaporated to solid residue. Then 1 ml of sulphuric acid and 2 ml of 2-chloroethyl alcohol cooled to –11 ºC were added. The solution was stirred and left for 15 min. After cooling to room temperature, 2 ml of n-hexane and, after light stirring, 5 ml of sodium sulphate were added to each tube. Each tube was shaken vigorously for 3 min and left until the separation of fractions. For chromatographic determinations, 1 ml of the hexane fraction was collected from each tube.

3.4. Investigation of the Recovery Coefficient for Carbofuran

Preliminary investigations utilized the following sorption materials: FPP-15 filter cloth, quality absorbent paper No. 390, polypropylene melt-blown type unwoven cloth and polypropylene welding needled type unwoven cloth.

Initially, dichloromethane was used, and then acetone and diethyl ether as solvents for the extraction of carbofuran from the sorption materials. Preliminary investigations of carbofuran extraction with dichloromethane from samples made of FPP-15 filter cloth and quality absorbent paper (390) demonstrated that it could not be used as a solvent. In the case of investigating extracts from the FPP-15 filter cloth, the reason was their too oily consistency, which could damage the microsyringe when injecting the samples into the chromatograph column. The extracts from absorbent paper did not raise any objections, but further experiments with that sorption material were abandoned because of its low mechanical resistance.

Because it was impossible to use dichloromethane, there was an attempt at using another solvent, acetone. Extraction of carbofuran from FPP-15 filter cloth without the evaporation stage and with

evaporation to solid was carried out. Although the consistency of solutions after acetone extraction did not raise any objections and their determinations were carried out, because the necessity to determine low concentrations of carbofuran was taken into consideration, there was an attempt to adjust the conditions of extraction so as to obtain the lowest possible sample volume prior to chromatographic determinations (the end volume of the extract not exceeding 5 ml). Therefore, the use of another solvent was tested, diethyl ether, less aggressive towards the sorption materials than dichloromethane and acetone. After initial investigations, for practical reasons extraction with three portions of diethyl ether was used: 10 ml + 5 ml + 5 ml (for 0.5 min with each portion).

Carbofuran solution of 0.1 mg/ml concentration in acetone was applied onto the prepared sorption material samples placed in 100-µl, 0.5-ml and 2-ml glass tubes with adjusted stoppers. Tubes containing the samples were left until the next day. Then each sample was shaken consecutively in three portions of diethyl ether: 10 ml + 5 ml + 5 ml (for 0.5 min in each portion). The collected extract was evaporated to solid residue, which was then dissolved in 1 ml of acetone. The content of carbofuran in the extract was determined by chromatography.

During the investigation of the recovery coefficients, clean samples of sorption materials were also subjected to control extraction, and reference standard solutions of the following concentrations were analysed: 4.0, 6.0 and 10.0 µg/ml of dichlorvos in acetone, 0.1 and 0.15 µg/ml of cypermethrin in acetone, 0.01 mg/ml of 2,4-D in ethanol, 0.1 mg/ml of carbofuran in acetone.

4. RESULTS AND DISCUSSION

The recovery coefficient R was calculated from the following formula:

$$R = (A_E - A_K) / A_P \quad (1)$$

where A_E—peak area for the active ingredients on the chromatogram of the extract, A_K—peak area of the same retention time as the specific active ingredients on the chromatogram of the extract from a pure sorption material sample, A_P—peak area of the specific active ingredients on the chromatogram of the reference solution.

Figure 1 presents the obtained active ingredient retention coefficient values for the specific sorption materials.

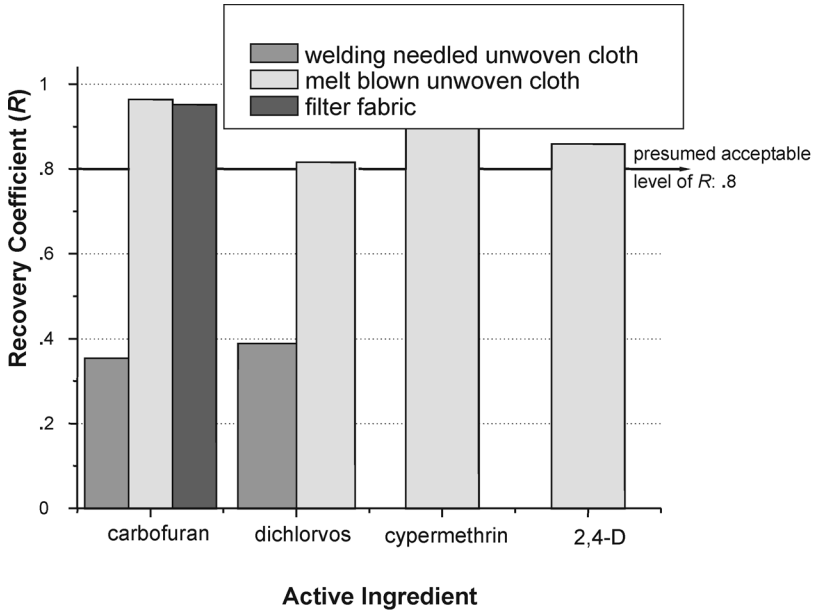

Figure 1. Values of the recovery coefficient (*R*) for active ingredients for selected sorption materials.

The obtained results were subjected to statistical analysis using the means test (t) against a constant reference value adopted in order to check whether the recovery coefficient obtained for a specific substance and a specific sorption material was actually higher than the presumed acceptable reference level of –0.8.

The analysis demonstrated that in the case of melt-blown type unwoven cloth, the t values were higher than the critical t distribution values for the given number of independent variables and the accepted significance level $\alpha = .05$ for all the analysed substances. Thus, it can be assumed with the probability $P = .05$ that the coefficients of recovery from unwoven cloth of such type for all four substances meet the pre-set criterion of ($R > .8$). Therefore, only that type of sorption material was taken into consideration in further analysis.

Further statistical analysis concerned the assessment of the effect of various volumes of active ingredient solutions applied onto samples of the selected sorption material (melt-blown type unwoven cloth). For this purpose, one-factor analysis of variance was performed for each individual substance (Figures 2, 3, 4, 5).

The analysis demonstrated that for cypermethrin, 2,4-D and carbofuran the solution volume applied onto a sorption material sample does not affect the value of the recovery coefficient (the values of F statistics are lower than the critical F distribution values at significance level $\alpha = .05$ for the given number of independent variables).

In the case of an active ingredient such as dichlorvos, the value of F statistics suggested the effect of the applied volume on the obtained recovery coefficient value. However, Scheffe's multiple comparison test did not confirm that thesis. No statistically significant differences between the analysed pairs of volumes were demonstrated for the accepted significance level $\alpha = .05$. Thus, the zero hypothesis that also in the case of dichlorvos the applied volume has no effect on the obtained recovery coefficient value should be maintained.

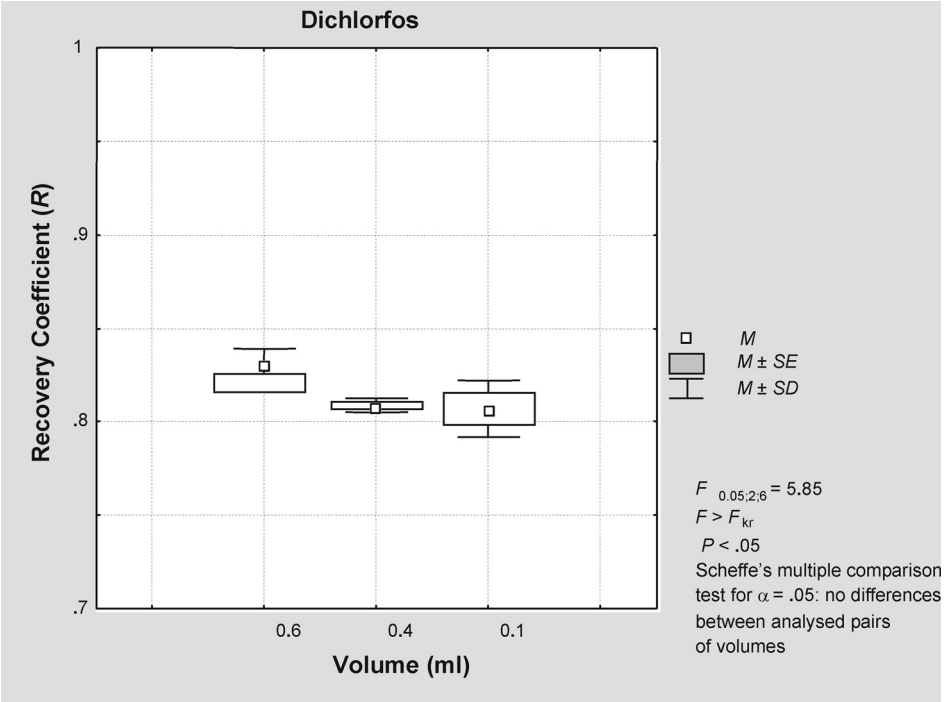

Figure 2. The dependence of the recovery coefficient (R) for dichlorvos on the volume of solutions applied onto samples of melt-blown type unwoven cloth.

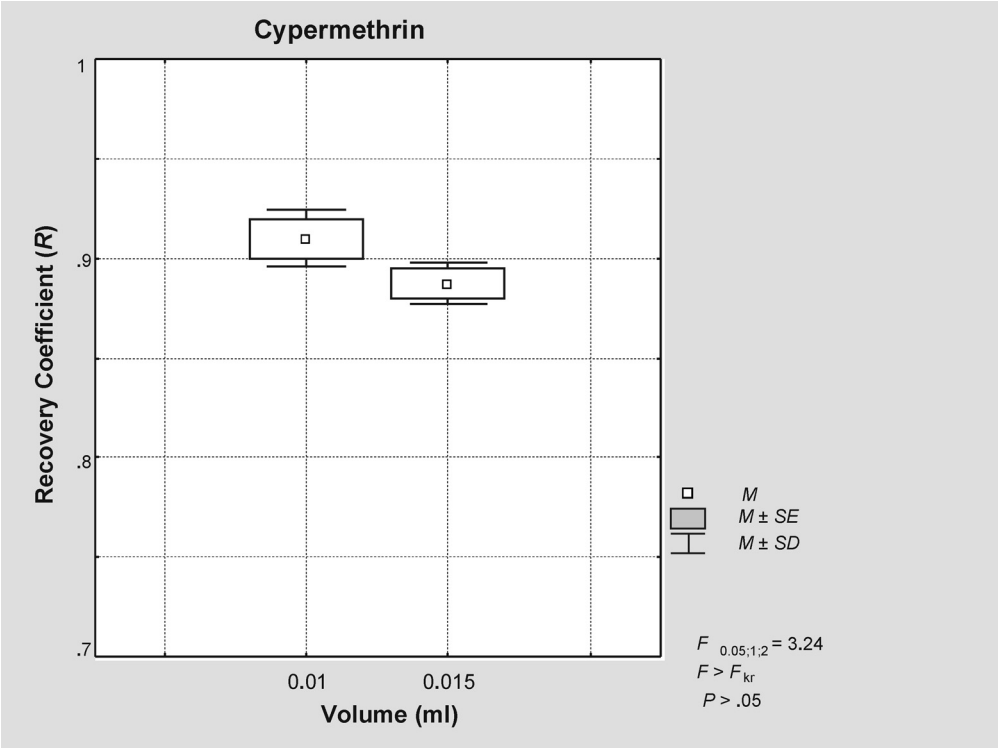

Figure 3. The dependence of the recovery coefficient (*R*) for cypermethrin on the volume of solutions applied onto samples of melt-blown type unwoven cloth.

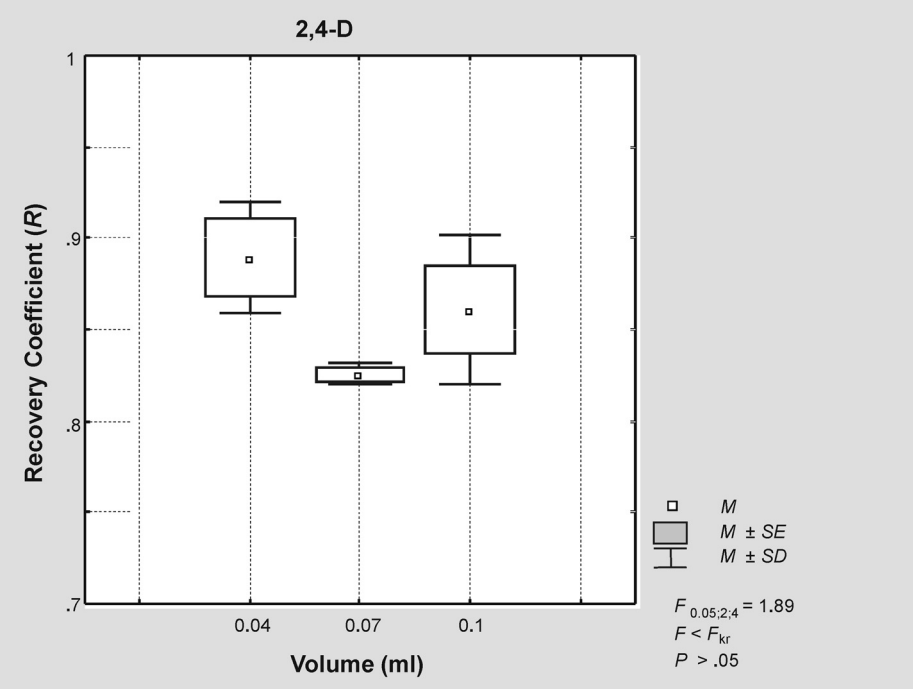

Figure 4. The dependence of the recovery coefficient (*R*) for 2,4-D on the volume of solutions applied onto samples of melt-blown type unwoven cloth.

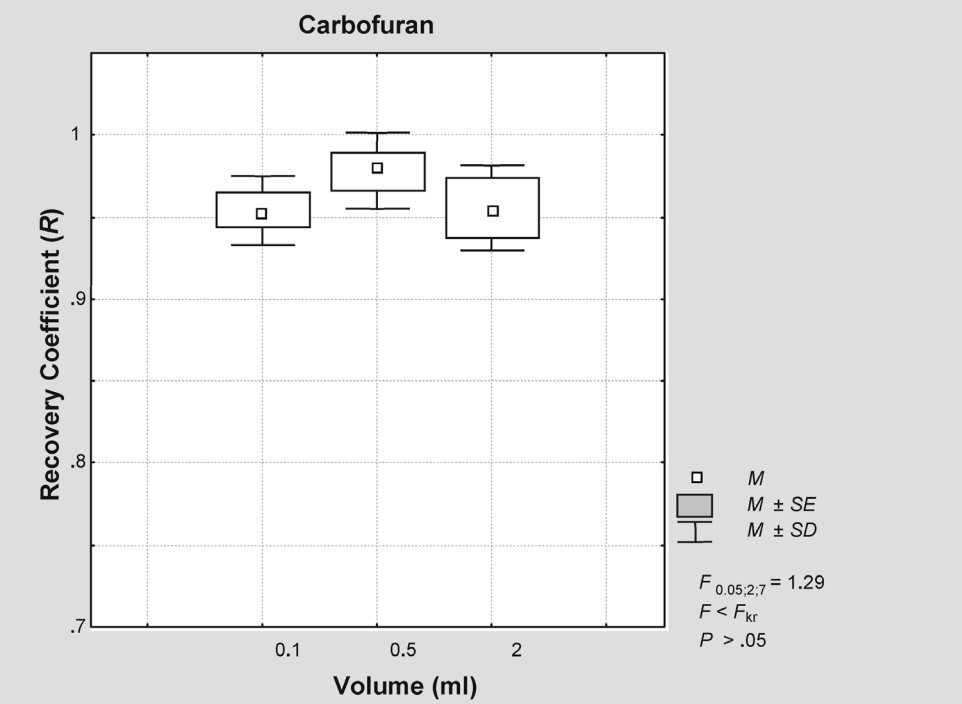

Figure 5. The dependence of the recovery coefficient (*R*) carbofuran for on the volume of solutions applied onto samples of melt-blown type unwoven cloth.

5. CONCLUSION

On the basis of the obtained results it was concluded that polypropylene melt-blown type unwoven cloth is characterized by the best sorption parameters and it can be used as a sorption material for selected active ingredients.

The study has demonstrated that polypropylene melt-blown type unwoven cloth is characterized by high recovery coefficient values for all four active ingredients proposed for the study. The highest recovery coefficient, .97, was obtained for carbofuran. The recovery coefficients obtained for the remaining three substances were lower and reached .89 for cypermethrin and 2,4-D, and .84 for dichlorvos.

The completed process of selecting the sorption material makes it possible to apply the developed methods of the chromatographic determination of the aforementioned substances for investigating the resistance of protective clothing materials to permeation by liquid pesticides.

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