Table 5. Limit of Detection and Guaranteed Limit of Detection Values for Different Apparatus Techniques

Parameter	Cd		Mo	
	AAS 1N	Perkin—Elmer	AAS 1N	Perkin—Elmer
$\rho(X_L)/$ (mg dm^{-3})	0.2	0.002	2.0	0.001
$\rho(X_G)/$ (mg dm^{-3})	0.3	0.005	4.0	0.003

were obtained. This fact is most probably due to the optical properties of the mentioned apparatus, as well as to the performance of the complex atomization process including preparation of aerosol.

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Application of Solid-Phase Extraction to HPLC Determination of Carbamate Pesticides in Water

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A simple device for the preconcentration of carbamate pesticides from water samples was used for their determination. Solid-phase extraction was carried out on sorbents Separcol SI C18 T and/or Porapak Q. The whole preconcentration procedure was optimized. Extracts were analyzed by RP-HPLC with UV detector on a column packed with Separon SGX-C18 in mobile phase methanol—water.

The quantitative determination of pesticides in water is important for the protection of environment. The analysis of pesticides in natural samples cannot be carried out, as a rule, without the appropriate concentration and clean-up process. The reviews of principles and applications of individual procedures can be found in many papers [1—5].

The application of multiresidual procedures in the analysis of pesticides is reported by *Ambrus* and *Thier* [6]. This paper is devoted to the sample preparation, extraction process, clean-up process of extract, and conditions for chromatographic determination. *Ambrus et al.* [7] describe the common method of the determination of pesticide residues, too.

The choice of concentration methods depends on the nature of compounds analyzed, concentration factor required, and the method of sample analysis.

The liquid-phase extraction used earlier has been recently replaced by the solid-phase extraction. The organic porous sorbents based on styrene—divinylbenzene, styrene—methacrylate or ethylene glycol—methacrylate copolymers or fluorinated polymers are used for the preconcentration of pesticides. The possibilities of the porous organic polymers application to the trace amount extraction of organic compounds from water are reviewed by *Dressler* [8]. Sorbents prepared by the chemical modification of silica gel by introduction of alkyl, cycloalkyl or aryl substituents are used frequently, octadecylsilica gel is used most frequently. *Tatar* and *Popl* [9] studied possibilities of preconcentration of triazine, phenoxycarboxylic acid pesticides, chlorpropham and triallate on sorbents Separon SE, Tenax GC, Porapak Q and Separon SI C18.

carbofuran

carbaryl

desmedipham

phenmedipham
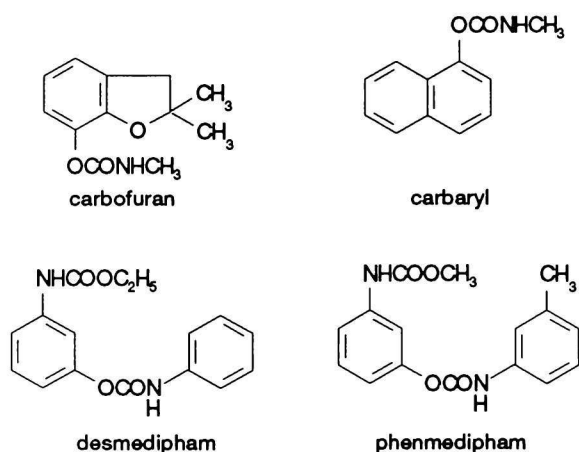
A lot of information about extraction and clean-up process is given in other papers [10—14]. Some information on preconcentration of carbamate herbicides was published before [15].

The volume of 20 to 2000 cm³ of water sample is usually analyzed at the flow rate 2 to 200 cm³ min⁻¹ (in dependence on the sorbent type). For the sorption of analytes 100 to 1200 mg of the sorbent are used. The volume of eluting solvent ranges within 0.1 to 5.0 cm³ according to the used type of the compounds analyzed. The recovery is usually over 80 % [16, 17].

Our paper deals with the optimized conditions for the determination of two carbamate insecticides (carbofuran and carbaryl) and two carbamate herbicides (phenmedipham and desmedipham) in water.

Separcol SI C18 T and Porapak Q sorbents were tested for preconcentration of pesticides. This preconcentration process was carried out by means of the device developed in our laboratory [18]. Eluates were analyzed by reversed phase (RP) HPLC.

EXPERIMENTAL

Acetone, methanol (both spectrophotometric grade), and distilled water repurified on a Separon SGX-C18 column were used as reagents. The standards of pesticides were as follows: carbofuran (FMC Chemicals, Geneva), carbaryl (Rhone-Poulenc, Philagro, Paris), phenmedipham, and desmedipham (Schering, Berlin). Sorption columns were packed with Separcol SI C18 T (Polymer Institute, Slovak Academy of Sciences, Bratislava), or Porapak Q (0.15—0.17 mm, Chrompack, Netherlands).

Liquid chromatograph 4002 with UV detector 4025 (Pye—Unicam, U.K.) set to 238, 220 and/or 210 nm, the chromatographic column (150 × 3.3 mm) packed with Separon SGX-C18 (5 μm; Tessek,
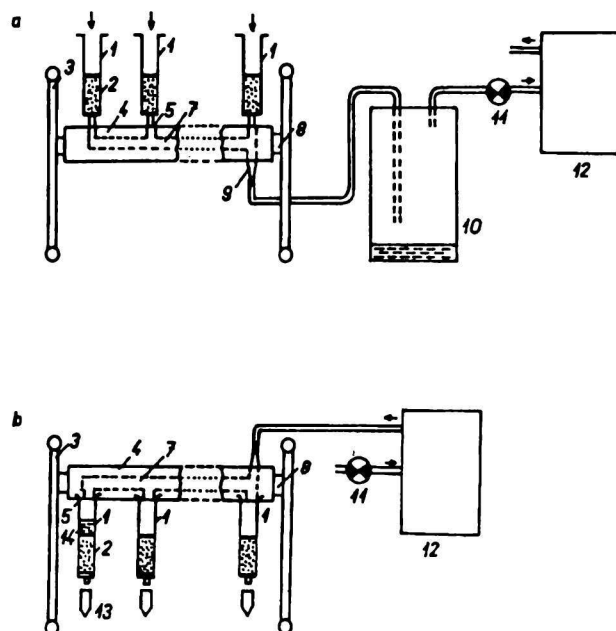

Fig. 1. Scheme of the total arrangement of the apparatus. a) Aspirating of samples, b) drying of sorbent, elution of pesticides. 1. Sorption columns; 2. sorbent; 3. metal stand; 4. block of multiextractor (teflon); 5. teflon inlet; 6. teflon cap; 7. drainage; 8. screw for fixation of teflon block on the stand; 9. inlet-outlet; 10. waste vessel; 11. flow controller; 12. pump; 13. vessel for capture of eluate; 14. eluting solvent; 15. capture of eluate; 16. additional teflon block; 17. sucking of air; 18. handle.

Prague), mobile phase methanol—water (φ_r = 1 0.6) at the flow rate 0.4 cm³ min⁻¹, and multiextractor [18] (Vojenský opravárenský podnik – 084, Olomouc) were used.

Sorption columns containing 100, 250, 500, and 1000 mg of the C18 sorbent, respectively or 300, 500, and 700 mg of the Porapak Q, respectively were successively conditioned by 1 cm³ of acetone, 1 cm³ of methanol, 2 cm³ of acetone, and 1.5 cm³ of distilled water. Water samples (50 to 1000 cm³) containing 0.2 to 1000 μg of pesticides were aspirated at the flow rate 5 cm³ min⁻¹ (arrangement in Fig. 1a). Then sorbent was dried by the flow of air and pesticides were eluted by 0.1 to 3.0 cm³ of acetone or methanol (arrangement in Fig. 1b). Eluates were evaporated to dryness in vacuum drier and the solid residues were dissolved in 60 mm³ of methanol. Portion of this solution (20 mm³) was analyzed by liquid chromatography.

RESULTS AND DISCUSSION

The multiextractor of modular type for solid-phase extraction has been developed. The whole arrangement of extraction apparatus used for pre-
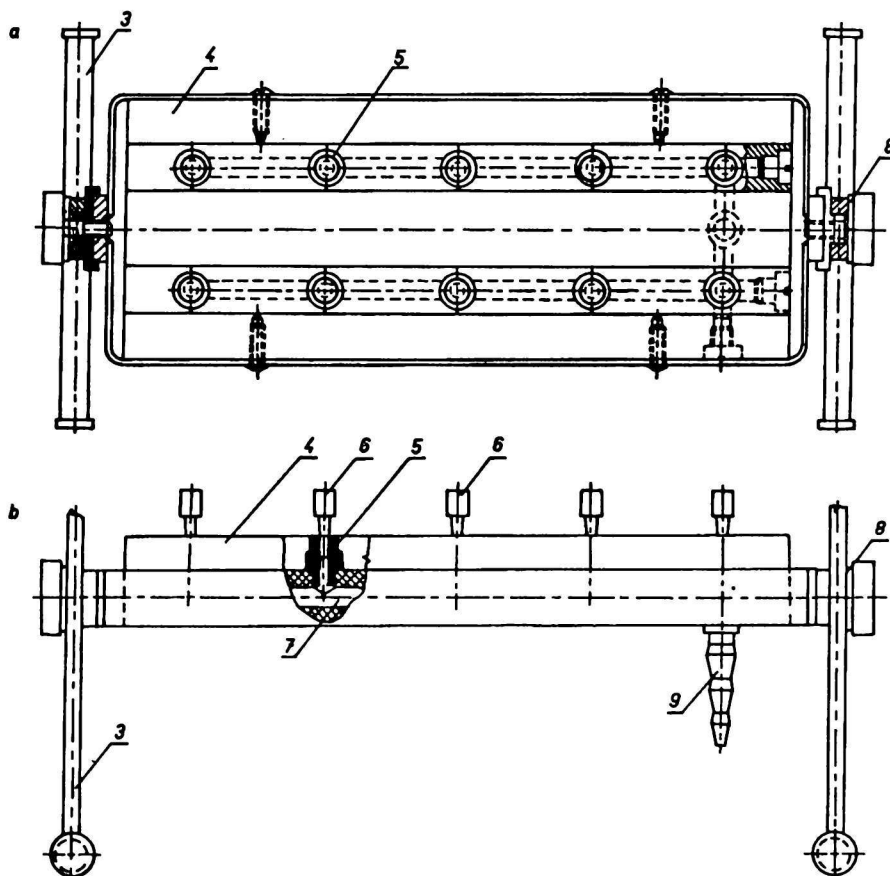
Fig. 2. Block of multiextractor. *a*) View from above, *b*) lateral view. The meaning of numbers is given in Fig. 1.

concentration of pesticides is given in Fig. 1. Details of multiextractor are presented in Fig. 2. In

case that the elution of pesticides cannot be carried out in arrangement shown in Fig. 1*b*, addi-
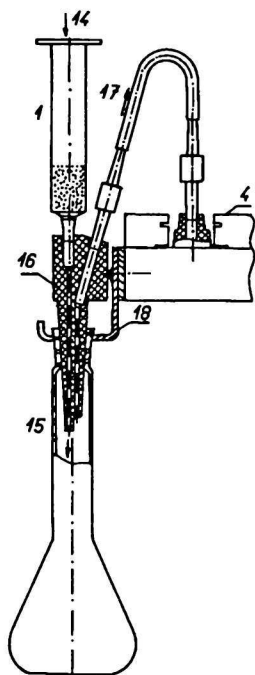

Fig. 3. Application of additional teflon block. The meaning of numbers is given in Fig. 1.
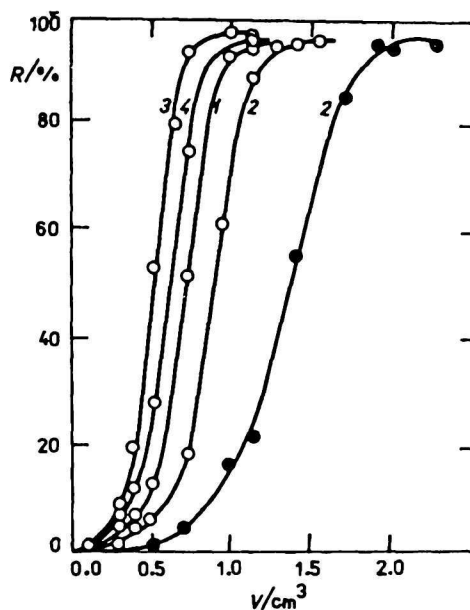

Fig. 4. Desorption curves of carbamate pesticides (*ca.* 5 µg in 50 cm³ of distilled water; 1000 mg of Separcol SI C18 T). ○ Elution by acetone, ● by methanol. *1.* Carbofuran; *2.* carbaryl; *3.* desmedipham; *4.* phenmedipham.
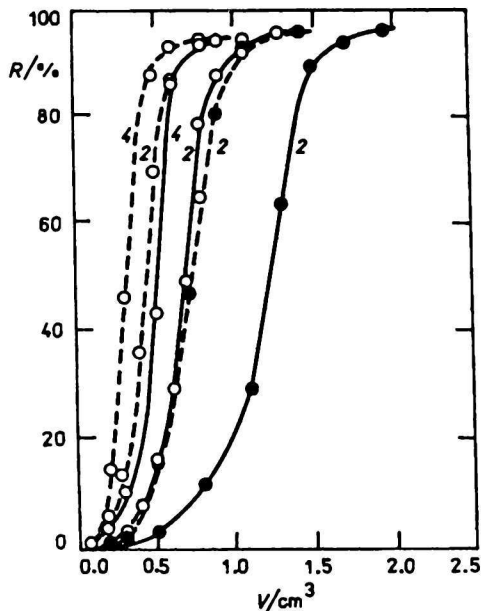
Fig. 5. Desorption curves of carbamate pesticides (5 μg in 50 cm^3 of distilled water) when using — 500 mg, ---- 250 mg of Separcol SI C18 T. ○ Elution by acetone, ● by methanol. *2.* Carbaryl; *4.* phenmedipham.
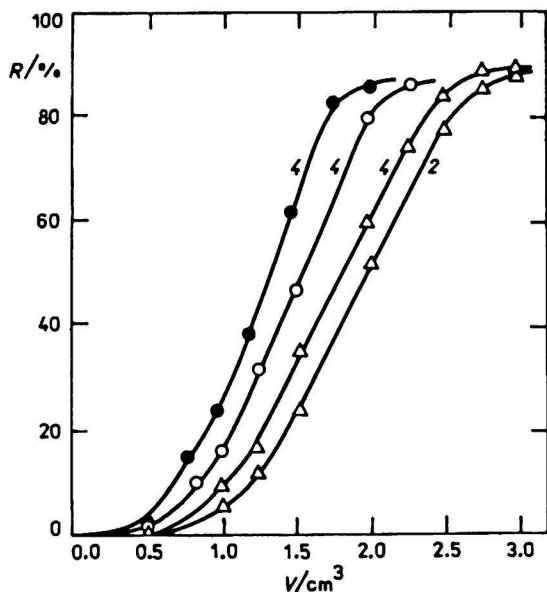
Fig. 6. Desorption curves of carbamate pesticides (5 μg in 50 cm^3 of distilled water) when using ● 300 mg, ○ 500 mg, △ 700 mg of Porapak Q sorbent (elution by acetone). *2.* Carbaryl; *4.* phenmedipham.

Fig. 7. Dependence of recovery on the flow rate of water sample (4.5 μg of carbofuran in 100 cm^3 of water) when using *a*) 1000 mg, *b*) 500 mg, *c*) 250 mg of Separcol SI C18 T (elution by acetone).

curves of individual carbamate pesticides obtained at elution with acetone or methanol from columns packed with various amounts of C18 sorbent. Fig. 6 shows the desorption curves for selected carbamate pesticides obtained at preconcentration on Porapak Q. In this case the elution of pesticides was carried out by acetone. As expected, the volume of eluting solvent necessary for the quantitative elution of pesticides decreases with decreasing amount of sorbent. Acetone is more effective eluting solvent than methanol for carbamate pesticides. With respect to greater consumption of eluting solvents Porapak Q is less suitable for preconcentration of carbamate pesticides than the modified silica gel (C18).

The flow rate of water samples does not influence the recovery up to values when $Q_V < 10$ to 15 cm^3 min^{-1} (in dependence on the C18 sorbent mass). The recovery in all tested C18 columns is reduced, if the flow rate exceeds 15 cm^3 min^{-1} (Fig. 7).
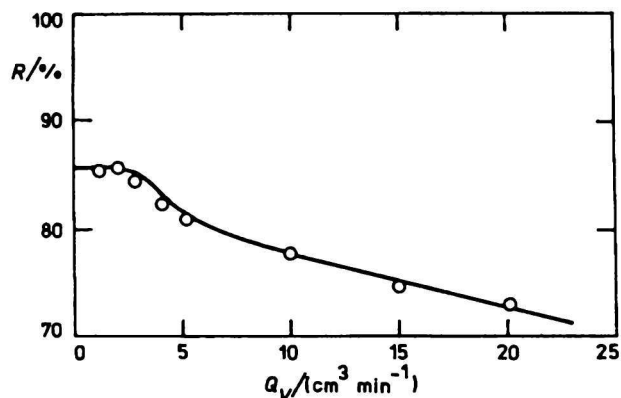
Fig. 8. Dependence of recovery on the flow rate of water sample (5.1 μg of carbofuran in 100 cm^3 of water, 500 mg of Porapak Q sorbent, elution by acetone).

tional teflon block (Fig. 3) can be joined to the block of multiextractor. This makes it possible to carry out the elution of pesticides at the arrangement of the apparatus as it is shown in Fig. 1*a* (aspirating of liquid) [19].

To find the minimum amount of eluent necessary for the quantitative desorption, elution curves were followed. Figs. 4 and 5 show the desorption
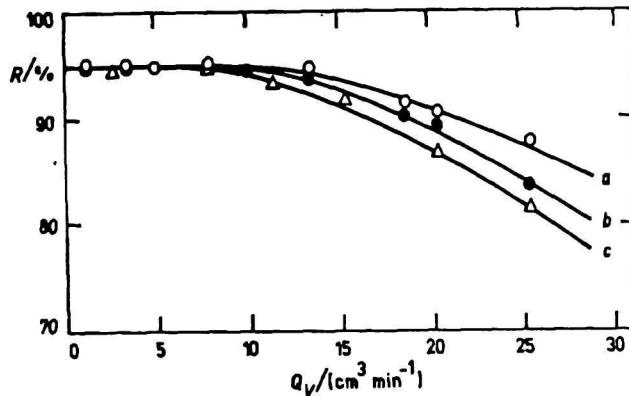
Similar test with Porapak Q showed that maximum allowed sample flow rate is 2 cm³ min⁻¹ (Fig. 8). The loss of recovery must be expected at the increased flow rate.

The recovery of pesticides in dependence on the volume of water sample, on the pesticides amount in it and on the sorbent mass (C18 and Porapak Q) is given in Tables 1—3.

Table 1 shows that in the case of using 100 mg of C18 sorbent it is possible to analyze less than

Table 1. Dependence of Recovery of Pesticide (5 μg of Carbofuran) on the Sample Volume and Sorbent Mass (Separcol SI C18 T)

Sorbent mass	Sample volume	Recovery	Sorbent mass	Sample volume	Recovery
mg	cm³	%	mg	cm³	%
100	50	93.54	250	500	86.36
250	50	94.11	500	500	93.12
500	50	95.23	1000	500	94.85
1000	50	95.18	250	1000	55.11
100	100	75.33	500	1000	82.16
250	100	93.89	1000	1000	94.17
500	100	95.11			
1000	100	94.99			

100 cm³ of sample. The decrease of the recovery was found when column was packed with 250 mg of C18 sorbent and sample volume was greater than 500 cm³. The volume 1000 cm³ of water sample can be analyzed on 1000 mg of C18 sorbent. The dependence of recovery on pesticides amount in water sample for C18 sorbent is given in Table 2. It is evident that the recovery considerably decreases with increasing amount of pesticides in water samples. The similar dependences were found even in the case of preconcentration of pesticides on Porapak Q. The results are given in Table 3.

Regression coefficient of the dependence between added and found amount of carbamate pesticides (0.3 to 15.0 μg of pesticides in 1000 cm³ of water) ranged from 0.9992 to 0.9995 with total standard deviations 0.072 to 0.125.

The limit of determination was calculated according to the relation $L = 10\,s_B$ where s_B is a standard deviation of blank. The limits of determination for carbofuran 0.25 μg dm⁻³ (measurement at λ = 210 nm), carbaryl 0.18 μg dm⁻³ (220 nm), desmedipham

Table 2. Dependence of Pesticides Recovery on their Amount (in 500 cm³) and Sorbent Mass (Separcol SI C18 T)

Pesticide amount	Sorbent mass	Carbofuran recovery	Carbaryl recovery	Desmedipham recovery	Phenmedipham recovery
μg	mg	%	%	%	%
10	1000	96.61	97.12	97.21	95.98
50	1000	95.99	97.90	98.91	94.74
100	1000	93.66	97.00	98.30	95.01
500	1000	62.36	67.34	65.86	66.30
1000	1000	41.79	35.31	27.93	29.81
10	500	95.13	96.89	97.83	95.88
50	500	95.05	97.48	97.37	95.00
100	500	95.52	96.03	97.11	94.76
500	500	62.14	51.11	47.53	49.18
1000	500	37.87	28.13	21.25	26.13

Table 3. Dependence of Pesticides Recovery on their Amount, Sample Volume, and Sorbent Mass (Porapak Q; Elution by Acetone)

Sorbent mass	Sample volume	Desmedipham Amount	Desmedipham Recovery	Carbaryl Amount	Carbaryl Recovery
mg	cm³	μg	%	μg	%
300	100	5.0	86.79	4.0	87.89
300	500	5.0	82.26	4.0	83.16
300	1000	5.0	63.70	4.0	61.36
500	100	5.0	86.11	4.0	86.32
500	500	5.0	87.36	4.0	88.44
500	500	20.0	85.93	40.0	85.86
500	500	80.0	85.19	120.0	84.30
500	500	300.0	50.88	480.0	52.26
500	1000	5.0	78.02	4.0	80.37
700	100	5.0	87.89	4.0	86.19
700	500	5.0	85.13	4.0	87.94
700	500	140.0	84.18	200.0	83.17
700	500	430.0	72.80	480.0	69.36
700	1000	5.0	85.48	4.0	84.99

0.17 μg dm⁻³ (238 nm), and phenmedipham 0.17 μg dm⁻³ (238 nm) were found.

Fig. 9 shows the chromatogram of extract of 1000 cm³ of drinking water with addition of 0.67—3.52 μg of carbamate pesticides. Preconcentration was performed on 1000 mg of Separcol SI C18 T, flow rate of the sample was 5 cm³ min⁻¹, the elution of carbamates was performed by 1.6 cm³ of acetone. Extract was evaporated to dryness, residue was dissolved in methanol and then analyzed by HPLC on the column packed with Separon SGX-C18 in mobile phase methanol—water. The detection was performed at λ = 220 nm. The HPLC analysis of extract was finished after 450 s. The separation of individual carbamates was satisfactory and undesirable substances were well separated from analytes.

From the results presented in our paper it follows that C18 sorbent is suitable for the
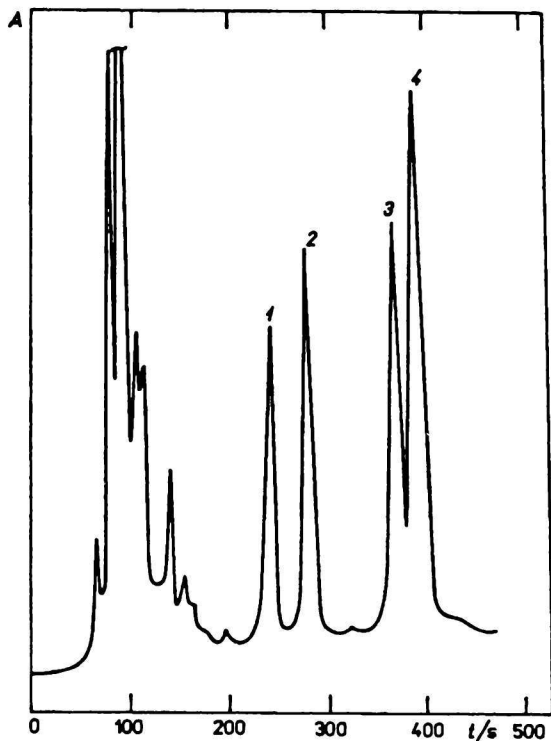
Fig. 9. Chromatogram of extract. *1.* Carbofuran; *2.* carbaryl; *3.* desmedipham; *4.* phenmedipham.

preconcentration of carbamate pesticides from water. On the other hand, Porapak Q seems to be unsuitable with respect to considerable dependence of the recovery of pesticides on the change of the sample flow rate even at the relatively low flow rates. Maximum values of the recovery under the optimized conditions are in comparison to Separcol SI C18 T lower.

After optimizing the principal parameters — amount and type of eluting solvent, sample flow rate, sorbent mass, volume of the sample with respect to the concentration of carbamates — it is possible to obtain very satisfactory results.

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Translated by S. Chromcová