

STUDY OF THE SORPTION OF SELECTED PESTICIDES ON NONPOLAR SORBENTS

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The break-through curves of aqueous solutions of selected pesticides were evaluated to determine the suitability of a number of nonpolar sorbents based on active carbon, synthetic polymers and modified silica gel for enrichment dilute aqueous solutions of these compounds. The best results were obtained using the styrene-divinylbenzene sorbents Aquapak 440A and Amberlite XAD-2, the styrene-ethylenedimethacrylate copolymer Separon SE and octadecyl silica gel materials. The effect of some experimental conditions on the sorption process, i.e. the flow rate of the sample through the column, the pesticide concentration in solution, the pH of the sorption medium, etc., was also studied. The results obtained are immediately applicable to the concentration of trace amounts of pesticides in water samples in sorption columns and also to chromatographic analysis by the HPLC method.

A number of approaches, based either on theoretical considerations or experimental results¹, can be employed to study the relationships between the properties of the solid and liquid phases during sorption. These include the break-through curve method, which yields practical, readily applicable information on the sorption process, especially in a dynamic column experimental arrangement. This method was used here to test various sorbents as column packings for concentrating dilute aqueous solutions of pesticides and their subsequent determination by high performance liquid chromatography, which is a widely used method for the analysis of these compounds^{2,3}.

THEORETICAL

Break-through (adsorption) curves are the graphical dependences of the concentration of the sorbed or desorbed substance in the eluate from the column on the volume of solution passed through the column or of the elution liquid. Evaluation of these curves reveals the suitability of the conditions used in the column sorption process, such as the sorbent particle size, flow rate of the liquid phase, minimal amounts of elutant for quantitative desorption, or the maximal amount of concentrated solution, or they can be used to calculate the sorbent capacity for the given compounds⁴⁻⁶ or their capacity ratios⁷.

It holds for the amount of solute m_s retained on a column with the sorbent from a solution with initial concentration c_0 that:

$$m_s = \int_{V_M}^{V_1} (c_0 - c) dV, \quad (1)$$

where c is the concentration of the substance in the eluate, V_1 is the volume passed through the column at the instant when the concentration of the substance prior to and after the column is identical (Fig. 1) and V_M is the dead volume of the column. For symmetrical curves (areas P_1 and P_2 in Fig. 1 are equal and it simultaneously holds that $(V_1 - V_b)/2 = V_{0.5}$), the value of m_s is usually calculated using the sample volume $V_{0.5}$ that has passed through the column at the instant when the concentration of the test substance in the eluate attains 50% of the initial value:

$$m_s = c_0(V_{0.5} - V_M). \quad (2)$$

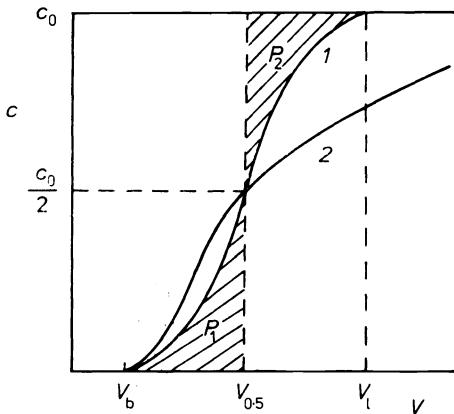


FIG. 1

Symmetrical (1) and unsymmetrical (2) break-through curves. c Concentration of the sorbed substance in the column eluate; c_0 concentration of the substance in the solution prior to the column; V eluate volume; V_b break-through volume of the sorbed substance; $V_{0.5}$ eluate volume for $c = c_0/2$; V_1 eluate volume for equal concentrations of the substance prior to and after the column; P_1 , P_2 areas characterizing the symmetry of the break-through curves

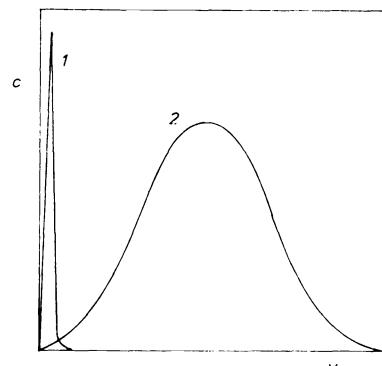


FIG. 2

Desorption curves. c Concentration of the desorbed substance in the eluate; V desorbate volume. Desorption agents: 1 suitable, 2 unsuitable

Symbol V_b denotes the volume of solution required for break-through of the test substance. The amount of solute adsorbed can also be determined by quantitative determination in the desorbate.

If the experiment is carried out in order to determine the capacity ratio, k , of the test substance in the given sorbent-liquid system, it is necessary to know the dead volume of the column, V_M :

$$k = m_s/(V_M c_0) . \quad (3)$$

It thus holds for symmetrical break-through curves that

$$k = (V_{0.5} - V_M)/V_M . \quad (4)$$

The shapes of the desorption curves reflect the suitability of the elution agent and the sorbent for quantitative desorption of the retained substances; for practical analytical reasons, the smallest possible volume of desorption agent is preferable (Fig. 2).

EXPERIMENTAL

Instruments and Apparatus

The instrumentation consisted of a single-stroke piston micropump, MC-706 (Mikrotechna, Prague), a two-stroke piston high-pressure pump, M 6000, apparatus for introducing the sample into the column, U6K, an M 440 double-beam photometric UV detector, an R 401 differential refractometric detector (all from Waters Assoc., Milford, U.S.A.), and a TZ 4221 double strip chart recorder (Laboratorní přístroje, Prague). A Soxhlet extraction instrument with a 100 ml distillation flask and stainless steel columns (sorption I—III; I: 40 × 2.3 mm, II: 150 × 3.2 mm, III: 130 × 13.5 mm, analytical 300 × 4.2 mm) were also used.

Chemicals and Sorbents

Methanol for UV, p.a. chemicals (all from Lachema, Brno) and redistilled water were used. The packings of the sorption columns are given in Table I. The packing of the analytical column: Silasorb C18, 10 µm, carbon contents 14.12% (Lachema, Brno). Pesticide standards: metoxuron (N'-(3-chloro-4-methoxyphenyl)-N,N-dimethyl urea), simazin (4,6-bis(ethylamino)-2-chloro-1,3,5-triazine), and 2,4-D (2,4-dichlorophenoxy acetic acid). Standards were obtained from the Central Control and Testing Agricultural Institute in Brno.

Procedure

Sorbent purification. The sorbents were extracted in the Soxhlet apparatus using 100 ml of the following solvents: redistilled water, methanol, chloroform, methanol, in that order; the sorbent purity was verified by chromatographic analysis of the final methanol extract.

Column packing and measuring of the dead volume. Columns I—III were packed with dry Silipor 300 C18; the other sorbents were packed in column I and II as a suspension in methanol.

Column I and the analytical column were packed with Silasorb C18 using the suspension technique at a pressure of 50 MPa using special equipment. The packed columns were washed with methanol, water and their dead volumes V_M were measured. Weakly basic anion exchanger Spheron DEAE-1000 was swollen in water and washed with 1M-NaOH and water and then converted to the NO_3^- form using 5M-LiNO₃; a suspension of the anion exchanger obtained in water was transferred to column I using an injection syringe.

The dead volume of the analytical column and columns II and III were found by measuring the elution volume of D₂O in water as the mobile phase with refractometric detection. The dead volume of column I was measured using three methods based on the following relationships:

$$V_{MI} = (m_1/m_{III}) V_{MIII} \quad (5)$$

$$V_{MI} = (V_1/V_{III}) V_{MIII} \quad (6)$$

$$V_{MI} = (m_1 - m_2)/(\rho_w - \rho_{\text{MeOH}}) \quad (7)$$

$$m_1 = m_1 - V_{MI}\rho_w; \quad m_1 = m_2 - V_{MI}\rho_{\text{MeOH}}, \quad (8)$$

where V_M is the dead volume of the column, m is the mass of sorbent in the column, V_{MIII} is the dead volume of column III measured by the elution method, V is the overall internal volume of the empty columns, m_1 and m_2 are the masses of column I packed with sorbent and water or methanol, respectively, and ρ_w and ρ_{MeOH} are the densities of water and methanol, respectively. The value of V_M for column I packed with Silasorb C18 was calculated from Eq. (6), referred to the analytical column with dead volume determined by the D₂O method. Analogously, Eqs (5) and (6) and column III as reference were employed in calculation of V_M for column II, Silipor 300 C18. The mass of Spheron DEAE-1000 packing was determined by weighing after removal from the column and drying. The values of m_1 and m_2 used to calculate V_M were determined as the arithmetic mean of three measurements.

Measuring of the break-through and desorption curves. Aqueous solutions of 10⁻⁶M metoxuron, 7 · 10⁻⁷M simazin and 10⁻⁵M 2,4-D were pumped by micropump MC-706 into the column containing sorbent that had been washed with methanol and water. 2,4-D acid was also sorbed from a medium of 0.4M-Na₂SO₄ and 0.1M-KH₂PO₄, pH = 3 (adjusted using H₃PO₄), where the column was prewashed with a liquid with the same composition as the sorption medium. After comparison of the solute concentration in the original sample and the eluate from the column, the retained substance was desorbed by elution with methanol.

The concentration of pesticide in the eluate from the column were measured by chromatographic analysis of the collected fractions with a volume of 5—25 ml on the Silasorb C18 analytical column with maximum sensitivity of the photometric detector (0.005 AU on the recorder scale) and a wavelength of 254 nm (metoxuron, simazin) or 280 nm (2,4-D), or by directly recording the break-through curves using this detector. The amounts of pesticides in the collected fractions were found using a calibration curve based on measuring of the heights of the chromatographic peaks. 2,4-D acid was eluted from Spheron DEAE-1000 ion exchanger using 5M-LiNO₃. The break-through curves were employed to determine the mass amount of desorbed pesticide, m_s ; these values and the V_M values for the columns were employed to calculate the capacity ratios of the sorbed substances for the given conditions.

The effect of the flow rate and the concentration of pesticides in water on the sorption process. The break-through curves of a 10⁻⁴M metoxuron solution were measured on column II containing Silipor 300 C18 at various linear flow rates of the solution through the column; the dependences of the capacity ratios, obtained by evaluation of the break-through curves, on the initial metoxuron concentration in water at constant flow rate were also measured.

TABLE I
Sorbents and their properties

Sorbent	Supplier	Composition	d_p μm	Mean pore diameter nm	Specific surface m ² g ⁻¹
Active carbon GA-1	Slovenské lučebné závody, Hnúšťa	Carbon	100–125	—	—
Amberlite XAD-2	Rohm and Haas	Styrene-divinylbenzene	100–160	8.5–9.0	290–330
Aquapak 40A	Waters Ass.	Styrene-divinylbenzene with sulfogroups	37–75	—	—
Separon SE	Laboratorní přístroje, Prague	Styrene-ethylenedimethacrylate	20–25	—	70
Silasorb C18	Lachema, Brno	RP C18 (14–12% C)	10	—	248 ^a
Silipor 300 C18	Lachema, Brno	RP C18 (15–71% C)	125–160	—	345 ^a
Spheron 1000	Lachema, Brno	Hydroxyethylmethacrylate- -ethylenedimethacrylate	40–63	—	—
Spheron DEAE-1000	Lachema, Brno	Hydroxyethylmethacrylate- -ethylenedimethacrylate with diethylamino groups	25–40	—	—
Synachrom E	Lachema, Brno	Styrene-divinylbenzene- -ethylvinylbenzene	200–250	9.0	520–620
Tenax GC	Appl. Science Labs	Poly(2,6-diphenyl- <i>p</i> - -phenylene oxide)	80–160	144	19–30

d_p Particle diameter; ^a specific surface of the original silica gel.

The determination of the reversibility of sorption and desorption. Volumes of aqueous solutions of metoxuron, simazin and 2,4-D at various concentrations, at which break-through does not occur (found from the break-through curves) were transferred to columns I and III packed with the test sorbent using micropump MC 706. 2,4-D acid was sorbed from 0.1M-KH₂PO₄ medium at pH = 3 (adjusted with H₃PO₄); 0.4M-Na₂SO₄ was also employed for column III packed with Silipor 300 C18. Methanol was used as the desorption agent except for elution of 2,4-D from Spheron DEAE-1000 with 5M-LiNO₃. Quantitative chromatographic analysis by the method of calibration curves based on peak height measurement was employed to determine the contents of the pesticides in the desorbate and the recovery of them at sorption-desorption process was calculated.

Concentration of river water samples containing trace amounts of simazin. An amount of 100 ml of filtered water from the Elbe River containing 10⁻⁸ mol l⁻¹ simazin was pumped at a rate of 1 ml min⁻¹ into column I packed with Aquapak 440A; the sorbed herbicide was eluted with 1 ml of methanol at a rate of 0.5 ml min⁻¹ and the desorbate was diluted with redistilled water to a volume of 2 ml; 40 µl of this sample was analyzed on a Silasorb C18 column with methanol-water mobile phase, $\phi(\text{MeOH}) = 0.55$.

DISCUSSION

Columns I–III packed with dry Silipor 300 C18 were highly pressure-resistant and thus exhibited long-term stability of the sorbent column. Columns packed with a polymeric sorbent by the suspension technique had to be washed with water or methanol prior to the experiments; sorbent settling has to be compensated by addition of new sorbent. Amberlite XAD-2 and Aquapak 440A exhibited the highest column stability, while that of Spheron 1000 and Separon SE was lower and that of Spheron DEAE-1000 and active carbon was very low, with destruction and clogging of the column at pressures above 2 MPa. The columns of the other sorbents were stable in the pressure range employed, 2–4 MPa. The corresponding flow rates of the aqueous solutions through the column I were from 0.3 to 0.5 ml min⁻¹, with values of up to 1.5 ml min⁻¹ for XAD-2 and modified silica gel. The analytical column and sorption column I packed with Silasorb C18 were packed by the suspension technique at 50–60 MPa and exhibited very good stability of columns at working pressures of 10–18 MPa.

Measuring the Column Dead Volume

Measurement of the V_M values for the columns by determination of the elution volume of substance not retained, i.e. D₂O for the given experiments, yielded correct results for columns with V_M greater than 1 ml (analytical and sorption III). The experimentally determined extra-column contributions to V_M attained values of 0.02–0.05 ml, corresponding to an acceptable error for columns with $V_M = 3$ ml of 1–2%, but corresponding to an error of 30–50% for a column with $V_M = 0.1$ ml. Consequently, the V_M values for columns I and II were determined by comparing

the overall internal volumes of these columns with those of columns packed with the same sorbent whose V_M values were measured with sufficient precision by the elution method. The procedure for comparing the sorbent masses for these columns was similar, but is suitable only for columns packed by the dry method.

As comparison columns were not generally available, the V_M values for column I were determined by the third method — calculation from the difference between the mass of the column packed with the sorbent filled with water and methanol. Comparison of the V_M values for column I packed with Silasorb C18 and Silipor 300 C18 found by the second and third methods indicated that the dead volumes found by the third method do not differ by more than 5%. A survey of the V_M values for the individual columns is given in Table II, and are the arithmetic means of the results of three measurements.

Measuring of Break-through Curves and Comparison of Sorbents

The herbicides metoxuron, 2,4-D and in some cases simazin were employed in the experiments as representatives of widely used urea, phenoxycarboxylic and triazine pesticides. These substances were selected as those members of the given groups that are most soluble in water and thus hardest to extract from it. Consequently, conditions for effective sorption of these substances will thus mostly be suitable for retention of related compounds.

The break-through and desorption curves were measured on column I, permitting the experiments to be carried out in an acceptable length of time for all the sorbents and the results obtained can be used directly for utilization of these columns as preconcentration columns in liquid chromatography systems⁸. An aqueous solution flow rate of 0.5 ml min^{-1} ensured an acceptable pressure drop on the column ($1-3 \text{ MPa}$) and stability of the sorbent column.

The pesticide concentration was chosen so that it could be determined by chromatographic analysis of fractions of the column eluate or by direct photometric detection at maximum detector sensitivity. The latter method was employed for sorbents with low break-through volumes and steep break-through curves as otherwise the recordings of the detector signals were affected by variations in the baseline and interpretation of the curves was difficult. In such cases, the pesticide concentration was determined by quantitative chromatographic analysis in a $5-25 \text{ ml}$ eluate fraction.

Methanol was chosen as the desorption agent both because of its elution ability and also because it is miscible with water and constitutes a component of the mobile phase in reversed-phase chromatography, also used in "on-line" use of preconcentration columns in HPLC systems.

The desorption of the retained substance from the column was followed both by

TABLE II
Column properties

Type of column	<i>L</i> mm	<i>d_c</i> mm	<i>V_c</i> ml	Sorbent	Packing mass		<i>V_M</i> , ml		
					g	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
Analytical	300	4.2	4.156	Silasorb C18	—	3.10	—	—	—
Sorption III	130	13.5	18.394	Silipor 300 C18	12.186	11.53	—	—	—
Sorption II	150	3.2	1.206	Silipor 300 C18	0.820	0.82	0.78	0.760 ^e	—
Sorption I	40	2.3	0.166	Silipor 300 C18	0.105	—	0.095	0.104	0.112 ^e
				Silasorb C18	0.115	—	—	0.124	0.130 ^e
				Synachrom E	0.036	—	—	—	0.130
				Separon SE	0.067	—	—	—	0.104
				Spheron 1000	0.044	—	—	—	0.140
				Active carbon GA-1	0.092	—	—	—	0.136
				Aquapak 440A	0.075	—	—	—	0.133
				Tenax GC	0.053	—	—	—	0.144
				Amberlite XAD-2	0.063	—	—	0.109	—
				Spheron DEAE-1000	0.027	—	—	0.050	—

L Column length; *d_c* inner column diameter; *V_c* volume of empty column; *V_M* column dead volume. ^a Elution volumes for D₂O; *V_M* from Eq. (2); ^c Eq. (6); ^d Eq. (7); ^e *V_M* used in subsequent calculations.

continuous photometric detection of the eluate and by chromatographic analysis of eluate fractions, as the elution peak of the desorbed substances often exceeded the sensitivity range of the detector and recorder and the whole desorption process could not be recorded.

Tables III–VI give the results obtained by evaluation of the break-through and desorption curves and Figs 3 and 4 depict examples of curves. It can be seen that sorbents Synachrom E and Spheron 1000 are completely unsuitable as packing materials for column I as the pesticides pass through the column with the first eluate fraction, and that GA-1 active carbon is also not suitable as the recovery of the pesticide is incomplete (2,4-D acid could not be desorbed even using 1M-NaOH or 7M-NH₄OH). The other sorbents can be used for concentration of these substances under certain conditions (the suitability of the sorbent is given by a high capacity ratio value and also by the break-through volume, see Tables III–VI).

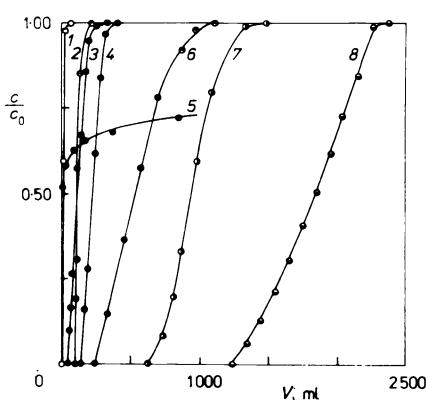


FIG. 3

Break-through curves for metoxuron on nonpolar sorbents. Column I; flow rate: 0.5 ml min^{-1} ; $c_0 = 10^{-6} \text{ mol l}^{-1}$. Sorbents: 1 Spheron 1000, 2 Silasorb C18, 3 Tenax GC, 4 Silipor 300 C18, 5 Synachrom E, 6 Amberlite XAD-2, 7 Separon SE, 8 Aquapak 440A. Other symbols as in Fig. 1

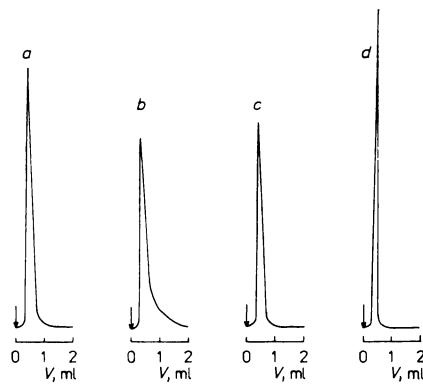


FIG. 4

Desorption curves of metoxuron and 2,4-D from column I packed with Amberlite XAD-2 and Silipor 300 C18. Flow rates for sorption and desorption: 0.5 ml min^{-1} ; desorption agent: methanol; c_0 (metoxuron) = $10^{-7} \text{ mol l}^{-1}$; c_0 (2,4-D) = $10^{-6} \text{ mol l}^{-1}$; V desorbate volume. a Amberlite XAD-2, concentration from 100 ml of 2,4-D solution in $0.1\text{M}-\text{KH}_2\text{PO}_4$, pH = 3; b Amberlite XAD-2, concentration from 100 ml of metoxuron solution in water; c Silipor 300 C18, concentration from 50 ml of 2,4-D solution in $0.1\text{M}-\text{KH}_2\text{PO}_4$, pH = 3; d Silipor 300 C18, concentration from 100 ml metoxuron solution in water

TABLE III

Parameters of the break-through and desorption curves for the sorption of 2,4-D from an aqueous solution with a concentration of 10^{-5} mol l⁻¹

Sorbent	V_b ml	$V_{0.5}$ ml	V_e ml	f	m_s mol	k_1	k_2
Silipor 300 C18	0.5	1.9	0.5	4	$2.3 \cdot 10^{-8}$	21	17
Synachrom E	0	6.0	—	—	—	—	46
Separon SE	30	64	—	—	$5.2 \cdot 10^{-7}$	499	615
Spheron 1000	0	0.5	1.0	0.5	$5.9 \cdot 10^{-9}$	4	3
Active carbon GA-1	>1 000	—	—	—	$1.0 \cdot 10^{-5a}$	>7 352	—
Aquapak 440A	2.0	6.5	0.5	13	$8.5 \cdot 10^{-8}$	64	49
Tenax GC	0	1.2	1.0	1.2	$2.1 \cdot 10^{-8}$	15	8
Amberlite XAD-2	1.5	8.6	—	—	$1.4 \cdot 10^{-7}$	131	79
Spheron DEAE-1000 ^b	300	350	5.0	70	$3.5 \cdot 10^{-5}$	6 900	7 000

^a Amount of 2,4-D retained from 1 000 ml of solution; ^b sorption from a 10^{-4} mol l⁻¹ 2,4-D solution, elution with 5M-LiNO₃. V_b Break-through volume; $V_{0.5}$ volume of sample passed so that the pesticide concentration in the eluate equals 50% of the initial value; V_e methanol volume required for desorption of 95% of sorbed pesticide; f orientative enrichment factor ($f = V_{0.5}/V_e$); m_s amount of pesticide retained on the column after equalization of its concentration prior to and after the column; k_1 capacity ratios calculated according to Eq. (3); k_2 capacity ratios calculated according to Eq. (4).

TABLE IV

Parameters of the break-through and desorption curves for the sorption of 2,4-D from 0.4M-Na₂SO₄ at a concentration of 10^{-5} mol l⁻¹

Sorbent	V_b ml	$V_{0.5}$ ml	V_e ml	f	m_s mol	k_1	k_2
Silipor 300 C18	5.0	36	1.1	33	$3.6 \cdot 10^{-7}$	317	321
Synachrom E	0	1.0	—	—	$2.7 \cdot 10^{-7}$	210	7
Separon SE	40	95	—	—	$9.5 \cdot 10^{-7}$	917	913
Spheron 1 000	0	3.5	—	—	$6.4 \cdot 10^{-8}$	46	25
Aquapak 440A	25	63	1.2	53	$6.5 \cdot 10^{-7}$	490	474
Tenax GC	0	7.6	1.0	7.6	$9.9 \cdot 10^{-8}$	69	53
Amberlite XAD-2	15	57	0.8	71	$6.2 \cdot 10^{-7}$	570	523

Symbols as in Table III.

Aquapak 440A exhibits the best properties for metoxuron and approximately a 1000-fold concentration of the original solution can be attained; Separon SE, Amberlite XAD-2 and Silipor 300 C18 are also useful. The best results for 2,4-D

TABLE V

Parameters of the break-through and desorption curves for sorption of 2,4-D from 0.1M-KH₂PO₄ (pH = 3) at a concentration of 10⁻⁵ mol l⁻¹

Sorbent	V_b ml	$V_{0.5}$ ml	V_e ml	f	m_s mol	k_1	k_2
Silipor 300 C18	25	83	1.2	69	9.4 · 10 ⁻⁷	841	741
Synachrom E	0	110	—	—	—	—	846
Separon SE	625	690	1.8	383	8.9 · 10 ⁻⁶	8 567	6 635
Spheron 1000	5.0	19	0.8	24	2.2 · 10 ⁻⁷	156	136
Aquapak 440A	525	665	1.8	369	6.4 · 10 ⁻⁶	4 827	5 000
Tenax GC	5	52	1.0	52	9.2 · 10 ⁻⁷	638	361
Amberlite XAD-2	140	410	1.5	273	4.5 · 10 ⁻⁶	4 110	3 761

Symbols as in Table III.

TABLE VI

Parameters of the break-through and desorption curves of metoxuron from an aqueous solution with a concentration of 10⁻⁶ mol l⁻¹

Sorbent	V_b ml	$V_{0.5}$ ml	V_e ml	f	m_s mol	k_1	k_2
Silipor 300 C18	140	230	1.2	192	2.0 · 10 ⁻⁷	1 786	2 053
Silasorb C 18	100	100	0.8	125	9.7 · 10 ⁻⁸	747	769
Synachrom E	0	2	—	—	3.2 · 10 ^{-7a}	2 446	15
Separon SE	650	940	2.0	470	9.6 · 10 ⁻⁷	9 230	9 038
Spheron 1000	0	6.6	0.7	9	6.7 · 10 ⁻⁹	48	47
Active carbon GA-1	>1 000	—	200 ^b	—	1.0 · 10 ^{-6a}	>7 352	—
Aquapak 440A	1 250	1 840	2.0	920	1.6 · 10 ⁻⁶	11 879	13 834
Tenax GC	50	120	1.2	100	1.3 · 10 ⁻⁷	882	833
Amberlite XAD-2	250	510	1.3	392	5.1 · 10 ⁻⁷	4 706	4 679

^a Amount of metoxuron retained by the sorbent from 1 000 ml of solution; ^b 65% recovery. Symbols as in Table III.

acid were obtained using sorption from a 0.1M-KH₂PO₄ medium, pH = 3; sorption from 0.4M-Na₂SO₄ is also effective. 2,4-D can be sorbed from neutral water on a column containing Separon SE, which is the best of the tested materials for this purpose. Aquapak 440A, Amberlite XAD-2 and Silipor 300 C18 can also be recommended. In order to evaluate the effect of KH₂PO₄ on the retention of 2,4-D, this herbicide was sorbed from water acidified with 1M-H₂SO₄ to pH = 3 on column I containing Aquapak 440A. The values of the capacity ratio $k_2 = 3440$ and the break-through volume $V_b = 400$ ml found in these experiments and compared with the values in Table V indicate that the increased retention of the acid on a nonpolar sorbent during sorption from buffered medium is also affected by suppression of acid dissociation and the salting-out effect of salts present. For the sake of completeness, it should be noted that 0.1–0.2 ml ($\sim V_M$ of column I) of distilled water forced through the column using an injection syringe are sufficient for washing the salts from the column prior to desorption of 2,4-D with methanol.

An amount of 0.8–2 ml of methanol is required to elute 95% of the retained herbicide for the individual sorbents; however, it should be borne in mind that the data in Tables III–VI correspond to elution of various amounts of herbicides. It has been found that a smaller amount of methanol is required for desorption of an amount that is smaller than the capacity of the sorbent. About 0.5 ml of this solvent suffices for quantitative elution in the concentration of 50–100 ml of a herbicide solution with a concentration of 10⁻⁷ to 10⁻⁶ mol l⁻¹ on columns packed with Aquapak 440A and Silipor 300 C18.

The amount of methanol required for 95% recovery of comparable amounts of metoxuron and 2,4-D from sorbents Amberlite XAD-2 and Silipor 300 C18 was compared (Fig. 4). It was found that this solvent is suitable for elution from RP C18; approximately twice the amount of methanol was required to extract the same amounts of substances from XAD-2.

The desorption of herbicides concentrated on columns I and II packed with Aquapak 440A and Silipor 300 C18 was studied. It can be seen from the data in Table VII that twice as much methanol was required to elute 95% of the simazin from an Aquapak 440A column as that necessary for the desorption of metoxuron or 2,4-D. These facts can be explained in terms of interactions of the amine nitrogens of simazine with the sulfo groups of the polymer, leading to increased retention. The desorption of metoxuron and simazin from Silipor 300 C18 proceeds in an identical manner.

The reversibility of the sorption–desorption process was tested on columns I and III for the studied sorbents. The sample volumes of metoxuron, simazin and 2,4-D solutions were chosen on the basis of the determined break-through volumes to avoid break-through of the pesticide and so that, where possible, these volumes would be the same for all the sorbents in a given column. The pesticides were determined in the methanol extract by quantitative chromatography and the recovery

was found (Table VIII). A recovery of greater than 90% was found in all cases, and values of 96–100% were mostly obtained. The only exception was active carbon, from which none of the pesticides could be eluted with acceptable efficiency.

TABLE VII

Dependence of the described amount of pesticide from Aquapak 440A (column I) on the volume of elution agent

Methanol volume, ml	Fraction desorbed, %		
	metoxuron	simazin	2,4-D
0.12	2.6	1.4	2.3
0.24	88.3	4.0	77.0
0.36	98.7	18.1	98.8
0.48	100.0	40.5	100.0
0.60	100.0	65.2	100.0
0.72	100.0	83.5	100.0
0.84	100.0	94.1	100.0
0.96	100.0	98.8	100.0
1.08	100.0	100.0	100.0

An amount of 25 ml of water ($\text{pH} = 3$) containing metoxuron, simazin and 2,4-D in amounts of 10^{-7} , 10^{-6} and 10^{-6} mol l^{-1} , respectively, concentrated at a flow rate of 1 ml min^{-1} . Desorption with methanol at a flow rate of 0.12 ml min^{-1} .

TABLE VIII

Dependence of the desorbed amount of pesticide from Silipor 300 C18 sorbent (column III) on the amount of elution agent

Methanol volume, ml	Fraction desorbed, %	
	metoxuron	simazin
10	—	28.5
20	—	73.4
25	94.1	—
30	—	98.8
50	99.1	100.0
75	99.9	100.0
100	100.0	100.0

Amount of pesticide adsorbed: $1.048 \cdot 10^{-3}$ mol metoxuron or $7.0 \cdot 10^{-5}$ mol simazin, flow rate during sorption and desorption with methanol, 5 ml min^{-1} .

The capacity ratio values for the herbicides on the columns were calculated in two ways: according to Eq. (3) yielding k_1 and according to Eq. (4) yielding k_2 . The k_1 and k_2 values were very similar (0–5%) for symmetrical break-through curves, but these differences increased with increasing asymmetry of the curves. The k_1 values are more accurate and precise. Table III–VI give a survey of the capacity ratios for metoxuron and 2,4-D.

The Effect of the Flow Rate on the Sorption Process

It follows from comparison of the shapes of the break-through curves for 10^{-4} M metoxuron on column III containing Silipor 300 C18 (Fig. 5) and the values calculated from these curves that a linear flow rate of the aqueous solution through the columns of 0.55 cm s^{-1} leads to a lower break-through volume and that the input and output pesticide concentrations become equalized after a longer time compared to a flow rate of 0.09 cm s^{-1} (the curves are less steep). This difference is a result of increasing resistance to mass transfer at higher flow rates. Simultaneously, the capacity ratio value is decreased (from 850 to 760), indicating nonequilibrium sorption at higher flow rates. It was confirmed in further experiments that the k values for metoxuron for solutions with the given concentration do not change in the flow-rate range 0.09 – 0.33 cm s^{-1} , corresponding to volume flow rates of 0.3 – 1.0 ml min^{-1} .

The Effect of the Concentration of the Sorbed Substance

The dependence of the capacity ratios of metoxuron on Silipor 300 C18 on the herbicide concentration in aqueous solutions was studied and the parameters of the break-through curves were evaluated (Table IX). The different k values for metoxuron for concentrations of 10^{-4} , 10^{-6} and 10^{-7} mol l $^{-1}$ indicate that the adsorp-

TABLE IX

Dependence of the parameters of the break-through curves on the metoxuron concentration on column II, Silipor 300 C18

c mol l $^{-1}$	V_b ml	$V_{0.5}$ ml	k_1	k_2
10^{-7}	1 200	2 340	2 850	2 850
10^{-6}	500	1 720	2 080	2 100
10^{-4}	450	590	760	780

Symbols as in Table III. Flow rate 1.8 ml min^{-1} .

tion isotherm is nonlinear in the given concentration range, as found in orientative experiments, the triazine herbicide simazin behaves similarly.

Concentration of River Water Samples Containing Trace Amounts of Simazin

Practical utilization of the results obtained in evaluation of break-through curves can be documented by the concentration of 100 ml of water from the Elbe River containing 10^{-8} mol l⁻¹ simazin on column I packed with Aquapak 440A. Figure 6

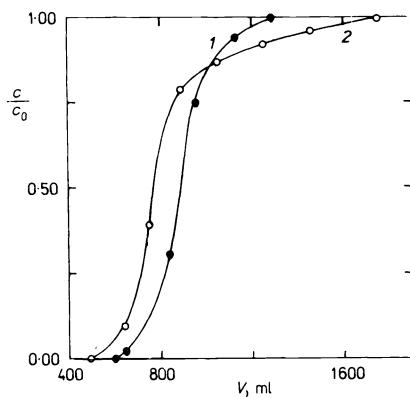


FIG. 5

Break-through curves of 10^{-6} mol l⁻¹ metoxuron on column II with Silipor 300 C18 packing at linear flow rates of 0.09 cm s⁻¹ (1) and 0.55 cm s⁻¹ (2). Symbols as in Fig. 1

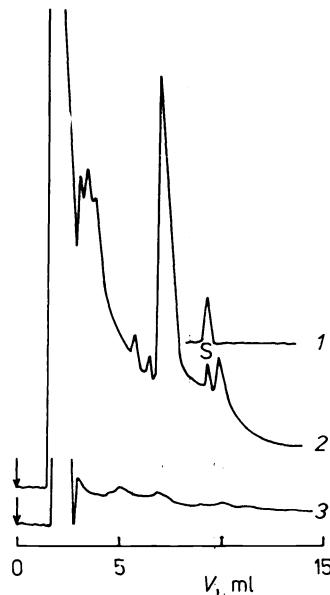


FIG. 6

Chromatographic analysis of the extract of 100 ml of river water containing added simazin in a concentration of 10^{-8} mol l⁻¹. Concentration conditions: column I, Aquapak 440A; flow rate 1 ml min⁻¹; desorption: 1 ml methanol, distilled water added to make a total volume of 2 ml. HPLC conditions: analytical column, Silasorb C18, 10 μ m, mobile phase: 55% (v/v) aqueous methanol; flow rate: 1 ml min⁻¹; detection UV, 254 and 280 nm, 0.005 AUFS; injected amount: 40 μ l. 1 Analysis of 10^{-6} mol l⁻¹ simazin; 2 analysis of the extract (S = simazin); 3 analysis of the unconcentrated simazin sample

TABLE X
Recovery of pesticides during concentration of aqueous solutions

Sorbent	Column	2,4-D				Metoxuron				Simazin			
		<i>u</i> cm s ⁻¹	<i>V</i> ml	<i>V_e</i> mol. .1 ⁻¹	<i>R</i> %	<i>V</i> ml	<i>V_e</i> mol. .1 ⁻¹	<i>R</i> %	<i>V</i> ml	<i>V_e</i> mol. .1 ⁻¹	<i>R</i> %	<i>V</i> ml	<i>V_e</i> mol. .1 ⁻¹
Silipor 300 Cl8	III	0.09	500 ^a	7.10 ⁻⁶	25 ^b	97.3	—	—	—	2000	7.10 ⁻⁶	25	94.4
	II	0.59	—	—	—	—	250	10 ⁻⁶	4.0	96.6	—	—	—
	II	0.59	—	—	—	—	250	10 ⁻⁷	2.5	99.8	—	—	—
	I	0.32	50	10 ⁻⁶	1.9	100.0	100	10 ⁻⁷	0.5	98.3	100	7.10 ⁻⁷	1.5
	I	0.32	—	—	—	—	—	—	—	100	4.10 ⁻⁷	1.3	99.5
Separon SE	I	0.32	50	10 ⁻⁶	3.0	100.0	50	10 ⁻⁷	0.5	99.4	—	—	—
Spheron 1000	I	0.24	10	10 ⁻⁶	1.0	102.0	—	—	—	—	—	—	—
Active carbon GA-1	I	0.25	1000	10 ⁻⁵	25	0	1000	10 ⁻⁶	200	65.0	1400	7.10 ⁻⁷	200
Aquapak 40A	I	0.25	100	10 ⁻⁶	1.5	106.0	100	10 ⁻⁷	2.7	98.7	—	—	—
Tenax GC	I	0.23	10	10 ⁻⁶	2.0	92.0	50	10 ⁻⁷	3.0	97.7	—	—	—
Amberlite XAD-2	I	0.31	100	10 ⁻⁶	2.0	100.0	100	10 ⁻⁷	3.3	100.0	—	—	—

V Sample volume; *c* pesticide concentration in the sample; *V_e* volume of the methanol extract; *R* recovery; *u* linear flow rate. Column dimensions see Table II. Flow rates through the columns (ml min⁻¹): I 0.5, II 1.8, III 5 ml min⁻¹. 2,4-D concentrated from 0.1M-KH₂PO₄ medium, pH 3. ^a 2,4-D concentrated from 0.4M-Na₂SO₄; ^b elution with 20% (v/v) methanol.

depicts the chromatogram of the desorbate. It was necessary to add 1 ml of water to 1 ml of the methanol extract prior to analysis, so that the ratio of the solvents is similar to that of the mobile phase in the chromatographic analysis (55% aqueous methanol). This procedure eliminated the appearance of "artefacts" on the chromatogram in the analysis of the methanol extract alone, facilitating interpretation of the recording. It is apparent from Fig. 6 that the presence of simazin can be demonstrated with fifty-fold concentration of the original water sample under the given experimental conditions, without further purification or concentration of the water extract. The pesticide recovery estimated from the peak heights for analysis of a standard solution and the methanol extract was about 95%.

Table X gives the recoveries of several pesticides for concentration from aqueous solutions on various sorbents. Various "on-line" arrangements for preconcentration columns in the system of liquid chromatograph, following from the results of these experiments, have already been published⁸.

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