LIQUID CHROMATOGRAPHY OF CARBAMATE, UREA, TRIAZINE, PHENOXYCARBOXYLIC AND ORGANOCHLORINE PESTICIDES

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The applicability of high performance liquid chromatography to the analysis of pesticide substances was tested using the Silasorb C 18 octadecyl silica gel stationary phase. The basic retention data were determined for 43 compounds of the title type and the optimum conditions for their chromatographic analysis were established. The results can be used in the determination of these substances in various environmental samples or in the quality control of commercial pesticide agents.

A number of chemical agents are used for protecting plants against animal pests, weeds and various diseases[1]. Among such pesticides, herbicides based on substituted ureas, triazines, phenoxycarboxylic acids and carbamates have found wide application, many of them also as effective insecticides. It is therefore pesticides of these types that attract particular attention of institutions dealing with the occurrence of foreing substances in the environment or in the various links of the food chain. In addition to the above groups, organochlorine insecticides are also of interest because of their high toxicity to higher organisms, their cumulative properties, high stability in the environment, and mutagenic and carcinogenic properties; although the use of many of them in agriculture has been banned, their residues are still encountered in the environment.

Most widespread for the analysis of pesticides are chromatographic techniques, particularly gas chromatography[2] and high performance liquid chromatography[2-4] (HPLC) which allow for a sufficiently sensitive and reliable determination of virtually all pesticides.

HPLC is given preference particularly for the determination of carbamates and phenoxycarboxylic acids and their salts, the gas chromatographic treatment meeting with some problems (thermal lability, need of derivatization). HPLC is also applicable to those groups of pesticides for which gas chromatography is more convenient as far as the sensitivity and selectivity of detection are concerned, e.g. organochlorine

or organosphosphorus compounds. A number of papers exist dealing with the HPLC determination of triazine[5-7], urea[8-10], carbamate[11-13], phenoxycarboxylic[14-16] and organochlorine[17-19] pesticides in waters, plants, animal tissues, soil and other material.

The majority of chromatographists prefer the reversed phase LC mode (nonpolar sorbent, polar mobile phase) for this purpose, although the normal phase mode using a polar sorbent and a nonpolar mobile phase can be used as well.

In the present work, pesticides from the groups mentioned were subjected to reversed phase HPLC treatment employing the Czechoslovak sorbent Silasorb C 18, a nonpolar chemically bonded octadecyl silica gel stationary phase; the aim of this work was to gain the relevant retention data and find a suitable wavelength for the UV detection, as a basis for the analysis of various samples containing the pesticides in question.

EXPERIMENTAL

Apparatus

The liquid chromatograph used comprised an M 6000 high pressure pump, an M 440 UV detector, an R-401 refractometric detector and a U 6 K injector (all from Waters Ass., Milford, U.S.A.); the apparatus was fitted with a 300 × 4·2 mm stainless steel column and was interfaced to a TZ 4221 two-line recorder (both from Laboratorní přístroje, Prague).

Chemicals

Methanol for UV spectroscopy, redistilled water, sodium sulfate crystalline p.a., potassium dihydrogen phosphate p.a., tetrabutylammonium hydrogen sulfate (TBAHS) p.a.

Silasorb C 18 sorbent 10 μm particle size (Lachema, Brno) was packed into the column by the high pressure slurry method; dead volume $V_M = 3{\cdot}10$ ml. Specific volume of the starting silica gel was 248 $m^2\ g^{-1}$ (manufacturer's data), bonded carbon content before and after additional silanization with trimethylchlorosilane was 13·53% and 14·20%, respectively.

Substances Treated

Urea derivatives: fenuron (N′-phenyl-N,N-dimethylurea), metoxuron (N′-(3-chloro-4-methoxyphenyl)-N,N-dimethylurea), MM (N′-(3-chloro-4-methylphenyl)-N-methyluera), diuron (N′-(3,4-dichlorophenyl)-N,N-dimethylurea), linuron (N′-(3,4-dichlorophenyl)-N-methoxy-N-methylurea), desfenuron (N′-phenyl-N-methylurea), deschlormetoxuron (N′-(4-methoxyphenyl)-N,N-dimethylurea), chlorbromuron (N′-(3-chloro-4-bromophenyl)-N-methoxy-N-methylurea), hydroxymetoxuron (N′-(3-chloro-4-hydroxyphenyl)-N,N-dimethylurea), neburon (N′-(3,4-dichlorophenyl)-N-butyl-N-methylurea), fluometuron (N′-(3-trifluoromethylphenyl)-N,N-dimethylurea), chlortoluron (N′-(3-chloro-4-methylphenyl)-N,N-dimethylurea), monolinuron (N′-(4-chlorophenyl)-N-methoxy-N-methylurea), metobromuron (N′-(4-bromophenyl)-N-methoxy-N-methylurea), isoproturon (N′-(4-isopropylphenyl)-N,N-dimethylurea), cycluron (N′-cyclooctyl-N,N-dimethylurea), BM (bis-N,N′-(3-chloro-4-methylphenyl)-urea).

Phenoxycarboxylic acids: PA (phenoxyacetic acid), 2,4-D (2,4-dichlorophenoxyacetic acid), MCPA (2-methyl-4-chlorophenoxyacetic acid), MCPP (2-(2-methyl-4-chlorophenoxy)propionic acid), 2,4-DP (2-(2,4-dichlorophenoxy)propionic acid), 2,4,5-T (2,4,5-trichlorophenoxyacetic acid), 2,4-DB (4-(2,4-dichlorophenoxy)butyric acid), MCPB (4-(2-methyl-4-chlorophenoxy)butyric acid), MDCPA (2-methyl-4,6-dichlorophenoxyacetic acid).

Carbamates and thiocarbamates: carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl-N--methylcarbamate), phenmedipham (O-(3-methoxycarbonylanilino)-N-(3′-methylphenyl)carbamate), desmedipham (O-(3-ethoxycarbonylanilino)-N-phenylcarbamate), methomyl (1-methylthio-O-(N-methylcarbamoyl)acetaldehydoxime), triallat (N,N-diisopropyl-S-2,3,3-trichloroallylthiocarbamate), thiofanox (3,3-dimethyl-1-methylthio-2-butanon-O-methylaminocarbonyloxime).

Substituted triazines: simazin (2-chloro-4,6-diethylamino-1,3,5-triazine), atrazin (2-chloro-4--ethylamino-6-isopropylamino-1,3,5-triazine), terbuthylazin (2-chloro-4-ethylamino-6-tert-butylamino-1,3,5-triazine), methoprotryn (2-methylthio-4-(3-methoxypropylamino)-6-isopropylamino-1,3,5-triazine), desmetryn (2-methylthio-4-isopropylamino-6-methylamino-1,3,5-triazine), prometryn (2-methylthio-4,6-diisopropylamino-1,3,5-triazine), terbutryn (2-methylthio-4-ethylamino--6-tert-butylamino-1,3,5-triazine).

Organochlorine compounds: aldrin (1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo*--5,8-exodimethanonaphthalene), dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a--octahydro-1,4-*endo*-5,8-exodimethanonaphthalene), *p,p′*-DDT (2,2,2-trichloro-1,1-bis-(4-chlorophenyl)ethane), lindan (γ-1,2,3,4,5,6-hexachlorocyclohexane).

Working Procedure

The retention characteristics of the pesticides were measured using methanol-water mobile phases; for phenoxycarboxylic acids, sodium sulfate, phosphate buffer or tetrabutylammonium hydrogen sulfate was added to this mobile phase system.

Samples in methanolic solutions or in solutions in the mobile phase system used, containing the substances chromatographed in concentrations on the order of 10^2 mg l^{-1}, were injected on column in volumes of 5—40 μl by means of the U 6 K injector; the mobile phase flow rate was adjusted to 1 ml min^{-1}. The eluate entered the photometric detector working simultaneously at 254 and 280 nm; for low-absorbing compounds, a refractometric detector was inserted in series with the photometric detector.

The retention volumes V_R were measured and the capacity ratios $k = (V_R - V_M)/V_M$ calculated. The results served to suggest suitable conditions for the isocratic chromatographic separation of pesticide mixtures. For the urea herbicides, the optimum conditions for their gradient elution[20] were also established. Determined were also the absorbance ratios at 280 nm to 254 nm (S^{280}_{254}) based on the peak heights.

RESULTS AND DISCUSSION

Phenoxycarboxylic Acids

Because of their dissociation ocurring during their chromatographic treatment if the mobile phase consists of aqueous methanol solely, the elution curves of the acids are nonsymmetrical and their retention is ill-reproducible. For this reason, either an electrolyte (Na_2SO_4) or the phosphate buffer of pH 3, or an ion pairing agent (tetrabutylammonium hydrogen sulfate) was added into the mobile phase.

Chromatography with mobile phase containing Na_2SO_4. The underlying principle of this approach is "salting-out" of the compounds from the polar mobile phase on the surface of the nonpolar phase by the action of the considerably better soluble electrolyte. In addition to an increase in the retention of the acids on the nonpolar octadecyl silica gel stationary phase, this effect brings about a considerable reduction in peak tailing[21].

The capacity ratios of the phenoxycarboxylic acids in 0·04M-Na_2SO_4 solutions in 40%–55% (v/v) methanol are given in Table I. The data along with the plot shown in Fig. 1 demonstrate that, as expected, the retention of all of the substances tested decreases with increasing methanol content of the mobile phase. Identically substituted acids are eluted in order acetic acid – propionic acid – butyric acid. Substitution by chlorine atoms and by methyl groups at the benzene ring increases the retention approximately to the same extent, which precludes mutual separation of pairs such as 2,4-D and MCPA, 2,4-DP and MCPP, or 2,4-DB and MCPB. Substitution by these substituents at the alkyl chains increases the retention to a lesser extent.

The Na_2SO_4 concentration used, 0·04 mol l^{-1} (chosen based on preliminary experiments), allows the volume fraction of methanol in the mobile phase to be varied over the region of 0–60% (v/v) (higher fractions lead to precipitation of Na_2SO_4), makes for a sufficient retention of the acids and suppresses their peak

TABLE I

Dependence of capacity ratios (k) of phenoxycarboxylic acids on the mobile phase composition

Substance	k					
	a	*b*	*c*	*d*	*e*	*f*
PA	0·449	0·272	0·191	0·121	0·607	0·617
2,4-D	4·322	2·489	1·761	1·086	2·688	2·651
MCPA	4·216	2·494	1·761	1·080	2·911	2·911
MCPP	6·956	4·006	2·730	1·623	4·632	4·476
2,4-DP	7·588	4·267	2·888	1·738	4·453	4·319
2,4,5-T	10·486	5·753	3·847	2·233	6·165	5·044
2,4-DB	18·020	9·274	6·903	3·615	7·083	6·666
MCPB	20·549	9·482	7·535	3·641	7·404	6·875
MDCPA	7·114	4·006	2·767	1·660	4·763	4·684

[a] 0·04M-Na_2SO_4 in 40% aqueous methanol; [b] 0·04M-Na_2SO_4 in 45% aqueous methanol; [c] 0·04M-$NaSO_4$ in 50% aqueous methanol; [d] 0·04M-Na_2SO_4 in 55% aqueous methanol; [e] 0·03M-KH_2PO_4 in 60% aqueous methanol, pH 3; [f] 0·005M-TBAHS in 60% aqueous methanol (all percentages v/v).

tailing. An example of separation of a mixture of five phenoxycarboxylic acids is shown in Fig. 2.

Chromatography with buffered mobile phases and ion pair chromatography. The former approach is based on a suppression of dissociation of the acids in the mobile phase owing to the presence of a buffer, whereupon the retention curves become symmetrical and the retention data well-reproducible; in the latter approach, the same goal is achieved by chromatographing the acids in the ion pair form. To make possible comparison of the two approaches with the above salting-out chromatography, mobile phases from which the acids are retained by Silasorb C 18 to an approximately identical extent were used. The capacity ratios of the phenoxycarboxylic acids in 0·03M-KH_2PO_4 in 60% (v/v) aqueous methanol at pH 3 (adjusted with H_3PO_4) and in 0·005M-TBAHS in the same aqueous methanol at pH 2·8 are given in Table I, while Table II summarizes, for all the three methods, the retention ratios $r_{i,s}$, which are the capacity ratios of the acids i relative to the capacity ratio of 2,4-D as the standard substance s. The selectivities of separation are mutually close in the three methods, hence, the structure effects discussed for the salting-out chromatography appear in the two other approaches to the same extent.

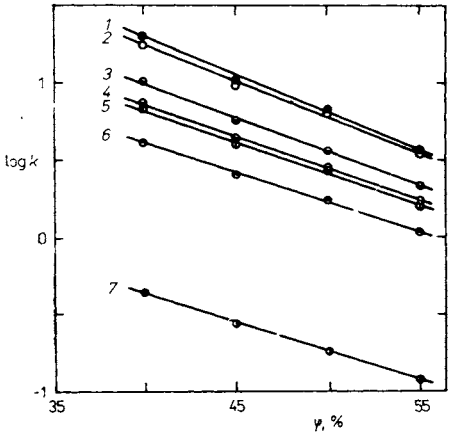

FIG. 1

Dependences of logarithms of capacity ratios k of phenoxycarboxylic acids on the methanol content of the mobile phase (0·04M-Na_2SO_4 in aqueous methanol). Solute: *1* MCPB, *2* 2,4-DB, *3* 2,4,5-T, *4* 2,4-DP, *5* MCPP, *6* 2,4-D, *7* PA

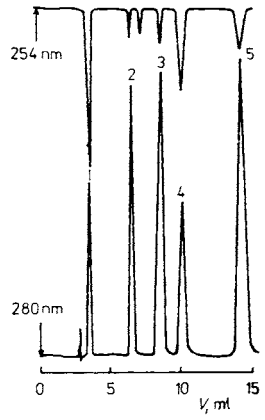

FIG. 2

Separation of a mixture of phenoxycarboxylic acids. Mobile phase: 0·04M-Na_2SO_4 in 55% (v/v) aqueous methanol, F_m = 1 ml min^{-1}. Detection at 254 and 280 nm, 0·1 a.u.f.s. Solute: 1 PA, 2 2,4-D, 3 2,4-DP, 4 2,4,5-T, 5 MCPB

Urea Herbicides

The capacity ratios of the substituted ureas in methanol–water mobile phases are given in Table III. Their retention increases with the number and size of the alkyl groups at the urea nitrogen, the contribution from a methoxy group being higher than that from methyl group (linuron, diuron), in agreement with published data[8]. The retention is increased by substitution by alkyl groups and halogen atoms at the benzene rings, methoxy groups having a smaller effect than methyl groups; hydroxy groups lower the retention appreciably. Owing to its high selectivity, the C 18 nonpolar phase is well suited to the mutual separation of urea herbicides as well as to chromatographic analysis of samples containing them. Separation of eight urea derivatives in the isocratic mode is shown in Fig. 3, while Fig. 4 shows a chromatogram obtained by gradient elution of a mixture of eleven urea herbicides under the optimum conditions, determined by calculation[20] and measured using an apparatus tested previously[22].

Triazine Herbicides

Similarly as with urea herbicides, the retention of triazine compounds decreases with increasing methanol content of the mobile phase (Table IV), although this decrease is somewhat less pronounced that for other pesticides (Fig. 5).

TABLE II

Retention ratios ($r_{i,s}$) of phenoxycarboxylic acids using various mobile phases; standard substance: 2,4-D

Substance	$r_{i,s}$		
	a	*b*	*c*
PA	0·109	0·226	0·233
2,4-D	1·000	1·000	1·000
MCPA	1·002	1·083	1·098
MCPP	1·609	1·723	1·688
2,4-DP	1·714	1·657	1·629
2,4,5-T	2·311	1·922	1·905
2,4-DB	3·726	2·635	2·514
MCPB	2·754	2·754	2·593
MDCPA	1·609	1·772	1·767

[a] 0·04M-Na_2SO_4 in 45% (v/v) aqueous methanol; [b] 0·03M-KH_2PO_4 in 60% (v/v) aqueous methanol; [c] 0·005M-TBAHS in 60% (v/v) aqueous methanol.

TABLE III

Dependence of capacity ratios (k) of urea-based herbicides on the concentration of methanol (φ) in the methanol–water mobile phase

Substance	Capacity ratio k at φ(MeOH), %						
	30	40	50	60	70	80	90
Hydroxymetoxuron	2·504	1·034	0·434	0·213	0·119	0·032	—
Fenuron	3·373	1·660	0·805	0·440	0·277	0·124	0·073
Metoxuron	9·985	3·725	1·572	0·744	0·389	0·150	0·083
MM	—	12·090	4·688	1·881	0·813	0·348	0·154
Diuron	—	20·225	7·508	2·866	1·222	0·491	0·226
Linuron	—	—	11·588	4·155	1·656	0·634	0·277
Chlorbromuron	—	—	13·888	4·812	1·860	0·696	0·287
Neburon	—	—	33·178	9·689	3·137	0·992	0·359
Desfenuron	—	1·451	0·721	0·440	0·226	0·113	0·053
Fluometuron	—	11·308	4·215	1·906	0·737	0·287	0·125
Chlortoluron	—	12·611	4·997	2·184	0·915	0·461	0·197
Monolinuron	—	10·108	4·006	1·906	0·813	0·359	0·176
Deschlormetoxuron	—	1·503	0·747	0·466	0·200	0·103	0·053
Metobromuron	—	13·446	5·571	2·437	0·992	0·420	0·208
Isoproturon	—	—	5·801	2·437	0·966	0·379	0·174
Cycluron	—	—	5·813	2·500	0·996	0·491	0·216
BM	—	—	—	—	8·296	2·126	0·665

TABLE IV

Dependence of capacity ratios (k) of triazine herbicides on the concentration of methanol (φ) in the methanol–water mobile phase

Substance	Capacity ratio k at φ(MeOH), %					
	40	50	60	70	80	90
Simazin	6·482	2·952	1·300	0·677	0·328	0·228
Atrazin	13·384	5·428	2·159	0·961	0·471	0·239
Terbuthylazin	—	12·383	4·125	1·606	0·675	0·383
Desmetryn	30·929	6·166	2·386	1·090	0·512	0·259
Methoprotryn	—	10·065	3·372	1·348	0·583	0·270
Prometryn	—	20·286	6·325	2·329	0·900	0·476
Terbutryn	—	24·553	7·389	2·587	0·992	0·414

From among the structural effects, the contributions from alkyl substituents at the amine groups can be assessed: the retention increases with their number and the chain length. Substitution by a methylthio group at the triazine ring raises the retention to a considerably greater extent than substitution by a chlorine atom. An example of separation of a mixture of triazine herbicides is shown in Fig. 6.

Carbamate Pesticides

The group of carbamate compounds studied comprises substances with highly different polarities. Table V and Fig. 5 demonstrate that the retention on the non-polar stationary phase differs accordingly. The dependence of the retention on the number and size of the alkyl and halogen substituents is again significant (methomyl, triallat). It is noteworthy that substitution by a methyl group at the benzene ring in the carbamate molecule contributes to the retention more than extending the alkyl chain at the carbamate oxygen by a homologous increment.

The separation of a mixture of five carbamate pesticides and impurities is shown in Fig. 7.

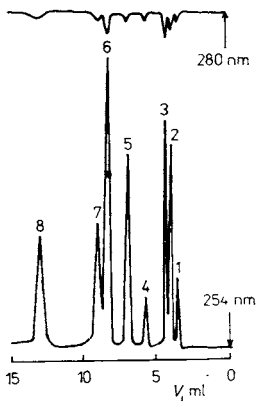

FIG. 3

Separation of a mixture of urea herbicides. Mobile phase: methanol–water (φ(MeOH) = = 70%), F_m = 1 ml min^{-1}. Detection at 254 and 280 nm, 1 a.u.f.s. Solute: 1 hydroxymetoxuron, 2 fenuron, 3 metoxuron, 4 MM, 5 diuron, 6 chlorbromuron, 7 neburon

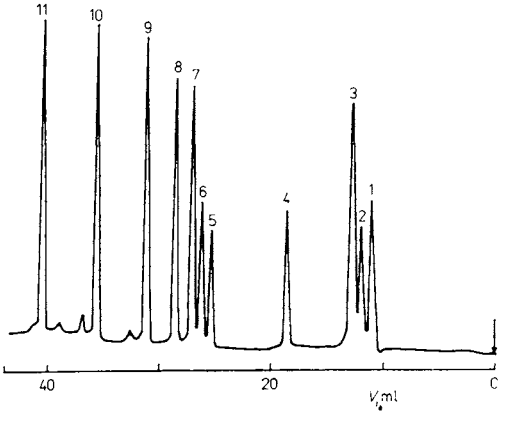

FIG. 4

Separation of a mixture of urea herbicides by gradient elution. Mobile phase: methanol–water, φ(MeOH) = 20%–100% (linear gradient 30 min), F_m = 1 ml min^{-1}. Detection: 254 nm. Solute: 1 hydroxymetoxuron, 2 desfenuron, 3 fenuron, 4 metoxuron, 5 isoproturon, 6 fluometuron, 7 chlortoluron, 8 diuron, 9 linuron, 10 neburon, 11 BM

Organochlorine Pesticides

Compounds of this class exhibit a higher retention than those of the other groups tested (Table VI). Their generally high capacity ratios are contributed to by the high number of chlorine atoms and presence of two aromatic rings or a bicyclic system in their molecules. The set of compounds was not extensive enough to permit the contributions from the structural units to the retention to be evaluated; only, a comparison of the chromatographic behaviour of aldrin and dieldrin reveals an appreciable retention lowering by the epoxy group oxygen.

Organochlorine pesticides can be conveniently separated from other substances (pesticides or other compounds present) on the octadecyl silica gel column using mobile phases with methanol contents exceeding 80% (v/v), where the majority of other pesticides or interferents are eluted virtually completely near the column dead volume. In such conditions, the individual chlorinated pesticides also are rather well separated (Fig. 8) owing to the relatively high differences in their polarities.

Detection

The 280 nm to 254 nm signal ratios for the pesticides are given in Table VII. The data allow us to draw some conclusions which may be of value particularly in the trace analysis of multicomponent samples. Characteristic is this ratio for phenoxycarboxylic acids for which, in contrast to the other pesticides, the absorbance at 280 nm is as much as 10 times higher than at the conventional 254 nm. The signal intensity ratio S_{254}^{280} nearly does not vary with the alkyl chain length for a constant benzene ring substitution while this ratio is affected appreciably by the type of the ring substituent. The highest values, 10·0–11·3, are observed for compounds with two chlorine atoms in the 2,4-positions (2,4-D, 2,4-DP and 2,4-DB); replacement of one of the chlorine atoms by a methyl group (MCPA, MCPP, MCPB) brings about lowering in this ratio to 7·2–7·4 while additional substitution by a chlorine atom (2,4,5-T) or a methyl group (MDCPA) leads to a decrease in S_{254}^{280} to 2·9 and 4·3, respectively.

For the urea herbicides, detection at 254 nm is convenient; many of them exhibit absorbances at this wavelength as much as 20 times higher than at 280 nm.

Triazine herbicides also absorb more at 254 nm than at 280 nm, although their S_{254}^{280} ratio is not as low as that of the ureas. Significant differences occur between chlorotriazines where $S_{254}^{280} = 0{\cdot}2-0{\cdot}3$ (decreasing with increasing length of the alkyl substituent at the amine nitrogen) and methylthiotriazines where S_{254}^{280} is about 0·1.

The absorption of radiation at 254 and 280 nm by the carbamate and thiocarbamate compounds is different in accordance with the diversity of their substituents. For methomyl, triallat and thiofanox, containing no aromatic system in their molecules, the S_{254}^{280} ratio is very low (0–0·15); for phenmedipham and desmedipham, com-

pounds with one benzene ring, the values are 0·27 and 0·30, respectively; and for carbofuran the value is increased as much as to 6·31 by the presence of the benzofuran system.

TABLE V

Dependence of capacity ratios (k) of carbamate pesticides on the concentration of methanol (φ) in the methanol–water mobile phase

Substance	Capacity ratio k at φ(MeOH), %						
	30	40	50	60	70	80	90
Methomyl	1·213	0·591	0·304	0·188	0·110	0·073	0·011
Triallat	—	—	—	—	9·426	2·780	0·869
Carbofuran	16·176	5·744	2·406	0·978	0·519	0·185	0·073
Thiofanox	—	9·277	3·817	1·513	0·677	0·297	0·093
Phenmedipham	—	—	9·534	2·907	0·935	0·353	0·113
Desmedipham	—	—	6·665	2·519	0·858	0·308	0·103

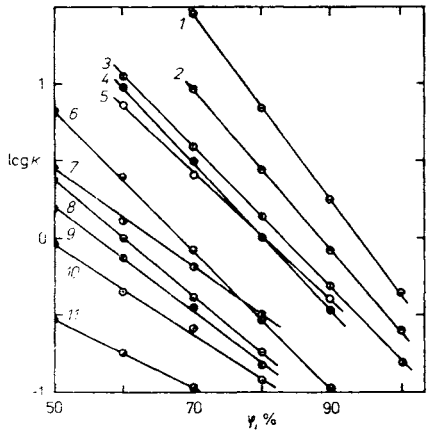

FIG. 5

Dependences of logarithms of capacity ratios k of some pesticides on the methanol content of the methanol–water mobile phase. Solute: *1* aldrin, *2* triallat, *3* lindan, *4* neburon, *5* terbutryn, *6* desmedipham, *7* simazin, *8* carbofuran, *9* metoxuron, *10* fenuron, *11* methomyl

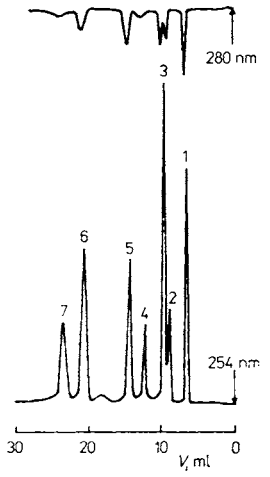

FIG. 6

Separation of a mixture of triazine herbicides. Mobile phase: methanol–water, φ(MeOH) = = 60%, F_m = 1 ml min^{-1}. Detection at 254 and 280 nm, 0·1 a.u.f.s. Solute: 1 simazin, 2 atrazin, 3 desmetryn, 4 terbutylazin, 5 methoprotryn, 6 prometryn, 7 terbutryn

From among the organochlorine pesticides analyzed, only *p,p'*-DDT absorbs at both wavelengths, whereas aldrin and dieldrin absorb UV radiation at 254 nm only. Together with lindan, they were detected conveniently by the refractometric detector

TABLE VI

Dependence of capacity ratios (k) of organochlorine insecticides on the concentration of methanol (φ) in the methanol–water mobile phase

Substance	Capacity ratio k at φ(MeOH), %				
	60	70	80	90	100
Aldrin	—	29·193	6·917	1·758	0·451
Dieldrin	—	11·053	3·086	0·931	0·256
p,p'-DDT	—	24·703	5·257	1·237	0·297
Lindan	11·003	3·826	1·401	0·502	0·154

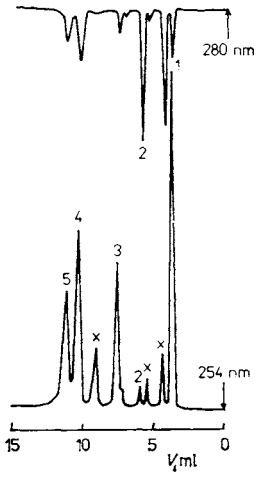

FIG. 7

Separation of a mixture of carbamate pesticides. Mobile phase: methanol–water, φ(MeOH) = 60%, F_m = 1 ml min^{-1}. Detection at 254 and 280 nm, 0·5 a.u.f.s. Solute: 1 methomyl, 2 carbofuran, 3 thiofanox, 4 desmedipham, 5 phenmedipham, x impurities

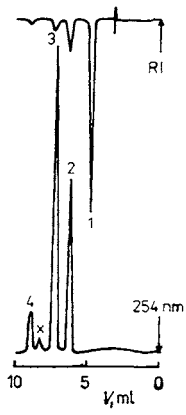

FIG. 8

Separation of a mixture of organochlorine insecticides. Mobile phase: methanol–water, φ(MeOH) = 90%, F_m = 1 ml min^{-1}. Detection at 254 nm and RI. Solute: 1 lindan, 2 dieldrin, 3 *p,p'*-DDT, 4 aldrin

in series with the photometric detector, working at 254 nm. This detection system was also used for the urea derivative cycluron, which – similarly as lindan – does not absorb at 254 or 280 nm. It should be, however, noted that refractometric detec-

TABLE VII

Absorbance ratios at 280 and 254 nm (S_{254}^{280}) in methanol–water mobile phases

Substance	S_{254}^{280}	Substance	S_{254}^{280}
	Ureas		
Hydroxymetoxuron	0·22	Fluometuron	0·17
Fenuron	0·10	Chlortoluron	0·11
Metoxuron	0·16	Monolinuron	0·05
MM	0·12	Deschlormetoxuron	0·18
Diuron	0·05	Metobromuron	0·04
Linuron	0·05	Isoproturon	0·09
Chlorbromuron	0·05	Cycluron	—
Neburon	0·05	BM	0·19
Desfenuron	0·17		
	Phenoxycarboxylic acids[a]		
PA	1·07	2,4,5-T	2·90
2,4-D	10·90	2,4-DB	11·3
MCPA	7·40	MCPB	7·3
MCPP	7·20	MDCPA	4·3
2,4-DP	10·00		
	Carbamates		
Methomyl	0·00	Thiofanox	0·15
Triallat	0·00	Phenmedipham	0·27
Carbofuran	6·31	Desmedipham	0·30
	Triazines		
Simazin	0·30	Methoprotryn	0·11
Atrazin	0·29	Prometryn	0·13
Terbuthylazin	0·22	Terbutryn	0·11
Desmetryn	0·11		
	Organochlorine compounds		
Aldrin	0·01	*p,p'*-DDT	0·16
Dieldrin	0·01	Lindan	—

[a] Mobile phase: 0·04M-Na_2SO_4 in aqueous methanol.

tion is generally at least an order of magnitude less sensitive than photometric detection and, moreover, nonselective, whereby its application to trace analyses, of complex samples in particular, is hampered. In such cases, UV detection at an appropriate wavelength or at two wavelengths simultaneously is more suitable. Knowledge of the absorbance ratios at these wavelengths, which are characteristic of the substances treated, can be of great help in the interpretation of chromatograms of complex mixtures.

It can be concluded that the Silasorb C 18 octadecyl silica gel stationary phase is well suited to the chromatographic analysis of the pesticides studied. Naturally, the capacity and retention ratios of the substances depend to a certain extent on the nature of the starting silica gel, degree of its coverage by the chemically bonded phase and the additional silanization of the free silanol groups, and so the data reported in this paper will vary with the sorbent production batch, the time the column has been in use and the column's previous history. These effects will be most marked in the case of substances containing basic groups, whereas for other substances they will not affect the reversed phase chromatographic results appreciably.

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