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LIQUID CHROMATOGRAPHY OF PHENYLUREA HERBICIDES AND RELATED COMPOUNDS ON CHEMICALLY BONDED ION-EXCHANGE MATERIALS

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SUMMARY

The possibilities of using new chemically bonded anion-exchange (Silasorb DEA) and cation-exchange (Silasorb S) materials for high-performance liquid chromatography of phenylurea herbicide compounds were investigated. The columns packed with Silasorb DEA or with Silasorb S ion-exchange materials can be used for efficient separations in normal-phase systems using *n*-propanol–*n*-hexane as mobile phases. Here, specific selectivity effects for phenylurea-type herbicides can be achieved in comparison to chromatography on unmodified silica or on chemically bonded aminosilica or cyanosilica, especially with Silasorb S columns. The influence of the mobile phase composition and of the structure of phenylurea herbicides on the chromatographic behaviour on Silasorb S and Silasorb DEA columns was investigated in detail and the possibilities of separation are illustrated by several examples.

INTRODUCTION

Organic solvents have often been used as mobile phase additives in ion-exchange chromatography in order to improve the peak shape and efficiency or to accelerate the elution of organic solutes from columns packed with ion-exchange resins based on an organic matrix (see, for example, the reviews[1–4]) or with chemically bonded ion-exchangers on a silica gel matrix[5,6]. Increased sorption of various simple aromatic compounds on cation- and anion-exchange resins in non-aqueous mobile phases was found in comparison to the sorption on unmodified polystyrene gels[7–12]. Sorption increases with the electronegativities of sample compounds and depends also on the ionic form of the anion exchanger[11].

It was possible to separate some positional isomers of simple aromatic compounds in these systems[12]. Significant retention of aniline and its derivatives was

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observed also on pellicular anion- and cation-exchangers[13]. The retention on ion exchangers in non-aqueous mobile phases has been explained by adsorption on the ion-exchange functional groups, which act as adsorption sites by formation of hydrogen bonds, chelates or charge-transfer complexes, or finally, by means of dipole–dipole interactions with the solutes[8–13], however, the affinity of the solutes towards the matrix of the ion exchanger may also contribute to the adsorption process[8,9].

In our previous investigations[14] of the separation of phenoxyacid herbicides it was found that aminopropyl bonded phases display interesting differences in selectivity when used in non-aqueous systems containing acetic acid in comparison to aqueous methanol acidic mobile phases. This observation stimulated further investigations using chemically bonded ion exchangers in non-aqueous mobile phases. The retention behaviour of phenylurea herbicides on chemically bonded anion- and cation-exchangers was compared to that on unmodified silica and on bonded amino- and cyanopropylsilica in non-aqueous systems containing *n*-propanol in *n*-hexane.

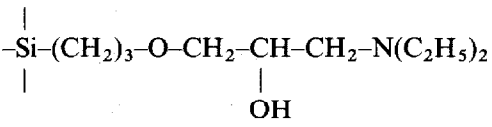
Most applications of high-performance liquid chromatography (HPLC) to separations of phenylurea herbicides in mixtures and to the determination of individual compounds in industrial products or in environmental samples make use of normal-phase chromatography on columns packed with unmodified silica[15–23], or of reversed-phase chromatography on columns packed with bonded alkylsilica materials[16–18,23–36] or with organic gels[37]. In addition to early attempts to separate phenylurea herbicides by column chromatography on liquid oxydipropionitrile as stationary phase[38], chemically bonded medium-polarity nitrile[25,35] and amino[22,39] stationary phases were successfully applied for this purpose.

EXPERIMENTAL

Unmodified silica gel Silasorb 300 and packing materials produced by its chemical modification, aminopropylsilica Silasorb Amine and cyanopropylsilica Silasorb Nitrile, were obtained from Lachema (Brno, Czechoslovakia). Samples of the cation exchanger Silasorb S and anion exchanger Silasorb DEA were prepared at the Research Institute of Pure Chemicals, Lachema, Brno, Czechoslovakia by chemical modification of Silasorb 300 using the following procedures.

End-capped 2-phenylethyl silica, prepared by silanization of Silasorb 300, was treated with chlorosulphonic acid in chloroformic solution. The resulting sulphonated cation exchanger contained 6.10% C and 1.90% S as determined by elemental analysis. The ion-exchange capacity was determined titrimetrically as 0.62 mmol/g.

Silasorb 300 was treated with 3-glycidoxypropyltrimethoxysilane to yield a product with 0.61 mmol/g of epoxide groups. This product was allowed to react with diethylamine in the second step and the final anion exchanger, a 3-(3-diethylamino-2-hydroxypropyloxy)propyl derivative of Silasorb 300, was obtained:



It contained 10.55% C and 0.79% N as determined by elemental analysis. The content of tertiary amino groups, which possess weak anion-exchange properties, was 0.58 mmol/g, as determined by non-aqueous titration with perchloric acid in acetic acid.

Stainless-steel columns were packed in the laboratory using a high-pressure slurry method. The column dead volumes, V_0, in non-aqueous mobile phases were determined as the elution volumes of *n*-heptane, which was not retained under the conditions used. The total porosities of the columns, ε_T, were calculated as the ratio of V_0 to the inner volume of the void column. The important characteristics of the packing materials and packed columns are listed in Table I.

The equipment used for chromatography included a Model 6000 pump, an U6K injector, a M 440 UV detector (all from Waters Assoc., Milford, MA, U.S.A.) and a PM 8010 recorder (Philips, Eindhoven, The Netherlands). The column dead volumes were determined using a Model R 401 differential refractometer as the detector (Waters Assoc.).

n-Propanol and *n*-hexane (analytical grade; Lachema) were used without further purification and the mobile phases were prepared by mixing these solvents in appropriate volume ratios.

Some of the chromatographed standard phenylurea herbicide compounds and other substituted phenylureas were obtained from various commercial sources. Others were synthesized at the department of Organic Chemistry, University of Chemical Technology, Pardubice, Czechoslovakia: 1 = N-phenylurea; 2 = N,N-diethyl-N′-phenylurea; 3 = N-phenyl-N′-isopropylurea; 4 = N-*n*-butyl-N′-phenylurea; 5 = N-*sec*.-butyl-N′-phenylurea; 6 = N-isobutyl-N′-phenylurea; 7 = N-methoxy-N-methyl-N′-phenylurea; 8 = N-benzyl-N′-phenylurea; 9 = fenuron (N′-phenyl-N,N-dimethylurea); 10 = desfenuron (N′-phenyl-N-methylurea); 11 = monuron (N′-4-chlorophenyl-N,N-dimethylurea); 12 = diuron (N′-3,4-dichlorophenyl-N,N-dimethylurea); 13 = chlortoluron (N′-3-chloro-4-methylphenyl-N,N-dimethylurea); 14 = N′-4-methyl-3-chlorophenyl-N-methylurea; 15 = metoxuron (N′-3-chloro-4-methoxyphenyl-N,N-dimethylurea); 16 = deschlormetoxuron (N′-4-methoxyphenyl-N,N-dimethylurea); 17 = isoproturon (N′-4-isopropylphenyl-N,N-dimethylurea); 18 = fluometuron (N′-3-fluoromethylphenyl-N,N-dimethylurea); 19 = neburon (N′-3,4-dichlorophenyl-N-*n*-butyl-N-methylurea); 20 = monolinuron (N′-4-chlorophenyl)-N-methoxy-N-methylurea); 21 = linuron (N′-3,4-dichlorophenyl-N-

TABLE I

PARAMETERS OF THE COLUMNS USED

l = Column length; d_c = column inner diameter; d_p = mean particle size; V_0 = column dead volume; ε_T = total porosity of the packed column; V_0, ε_T were determined as the mean values for 5–30% *n*-propanol in *n*-hexane as the mobile phases, using *n*-hexane as the dead volume maker.

Packing material	d_p (μm)	l (mm)	d_c (mm)	V_0 (cm³)	ε_T
Silasorb 300	10	300	4.6	4.12	0.83
Silasorb Nitrile	10	300	4.2	3.29	0.79
Silasorb Amine	10	300	4.2	3.25	0.78
Silasorb DEA	15	300	3.8	2.33	0.69
Silasorb S	10	300	4.2	2.63	0.63

methoxy-N-methylurea); 22 = metobromuron (N'-4-bromophenyl-N-methoxy-N-methylurea); 23 = chlorbromuron (N'-3-chloro-4-bromophenyl-N-methoxy-N-methylurea) and 24 = N,N'-bis(3-chloro-4-methylphenyl)urea.

RESULTS AND DISCUSSION

Chromatography of phenylurea herbicides and other substituted phenylureas on Silasorb S and Silasorb DEA in non-aqueous mobile phases

Influence of mobile phase composition on retention. Urea herbicides are neutral non-ionic compounds and their separation cannot proceed by an ion-exchange mechanism. However, in our earlier experiments, we found that modified Spheron anion- and cation-exchangers with an organic matrix were suitable for chromatographic separations of a number of non-ionic solutes, such as the bases of nucleic acids, nucleosides, alkaloids, barbiturates, sulphonamides and phenols, in aqueous meth-

TABLE II

RETENTION VOLUMES, V_R, AND CAPACITY FACTORS, k', OF SUBSTITUTED PHENYLUREAS AND PHENYLUREA HERBICIDES ON SILASORB S IN NON-AQUEOUS MOBILE PHASES

I = 15% *n*-Propanol in *n*-hexane; II = 20% *n*-propanol in *n*-hexane; III = 30% *n*-propanol in *n*-hexane; IV = 40% *n*-propanol in *n*-hexane.

Compound	*I*		*II*		*III*		*IV*	
	V_R (cm^3)	k'	V_R (cm^3)	k'	V_R (cm^3)	k'	V_R (cm^3)	k'
Fenuron	37.20	13.12	28.09	9.66	17.89	5.79	13.89	4.27
Desfenuron	–	–	39.69	14.09	22.89	7.69	17.56	5.66
Monuron	23.38	7.87	15.69	4.95	9.52	2.61	8.47	2.22
Diuron	14.87	4.64	11.01	3.18	7.37	1.80	5.78	1.19
Chlortoluron	17.63	5.69	13.72	4.21	9.06	2.44	7.03	1.67
N'-4-Methyl-3-chlorophenyl-N-methylurea	28.01	9.63	17.49	5.64	10.72	3.07	9.62	2.65
Metoxuron	–	–	35.13	12.33	19.70	6.78	18.02	5.84
Deschlormetoxuron	–	–	104.30	38.58	31.27	10.87	35.81	12.59
Isoproturon	25.83	8.80	16.15	5.13	11.94	3.53	10.86	3.12
Fluometuron	12.26	3.65	8.81	2.34	6.06	1.30	5.24	0.99
Neburon	6.90	1.62	5.05	0.92	3.99	0.51	3.78	0.43
Monolinuron	5.39	1.05	4.63	0.76	3.87	0.47	3.47	0.32
Linuron	5.47	1.08	4.44	0.68	3.64	0.38	3.61	0.37
Metobromuron	5.47	1.08	4.57	0.73	3.75	0.42	3.46	0.31
Chlorbromuron	5.54	1.10	4.70	0.78	3.74	0.42	3.35	0.27
N,N'-Bis(3-chloro-4-methylphenyl)urea	11.36	3.31	7.92	2.00	5.46	1.07	5.14	0.95
N-Phenylurea	–	–	–	–	105.99	39.22	141.40	52.66
N,N-Diethyl-N'-phenylurea	17.11	5.49	11.05	3.19	6.54	1.48	5.48	1.08
N-Phenyl-N'-isopropylurea	19.17	6.28	11.46	3.35	6.94	1.63	6.40	1.43
N-*n*-Butyl-N'-phenylurea	18.35	5.96	13.30	4.05	6.56	1.49	6.69	1.54
N-*sec*.-Butyl-N'-phenylurea	15.67	4.95	–	–	5.92	1.25	5.65	1.14
N-Isobutyl-N'-phenylurea	15.82	5.00	12.01	3.56	6.03	1.29	5.93	1.25
N-Methoxy-N-methyl-N'-phenylurea	4.90	0.86	4.32	0.64	3.58	0.36	3.27	0.24
N-Benzyl-N'-phenylurea	15.61	4.92	9.49	2.60	6.10	1.32	5.51	1.09

anol mobile phases without any ionic additives[40–42]. This can be explained by the simultaneous effects of: (a) polar interactions of solutes with the functional ion-exchange groups and (b) hydrophobic interactions, in which the organic matrix of the modified Spheron materials plays a similar rôle as the hydrophobic carbonaceous moieties of alkylsilica bonded non-polar phases.

We have found similar differences in retention of various phenylurea herbicides on Silasorb S and Silasorb DEA columns in mobile phases containing various amounts of *n*-propanol in *n*-hexane. The experimental capacity factors determined are given in Tables II and III.

The retention of phenylurea herbicides on the two modified Silasorb ion exchangers studied decreases with increasing concentration of *n*-propanol, *c*, in the mobile phase and the plots of log *k'* *vs.* log *c* are approximately linear at low concentrations (Figs. 1 and 2). This dependence is similar to that found in normal-phase

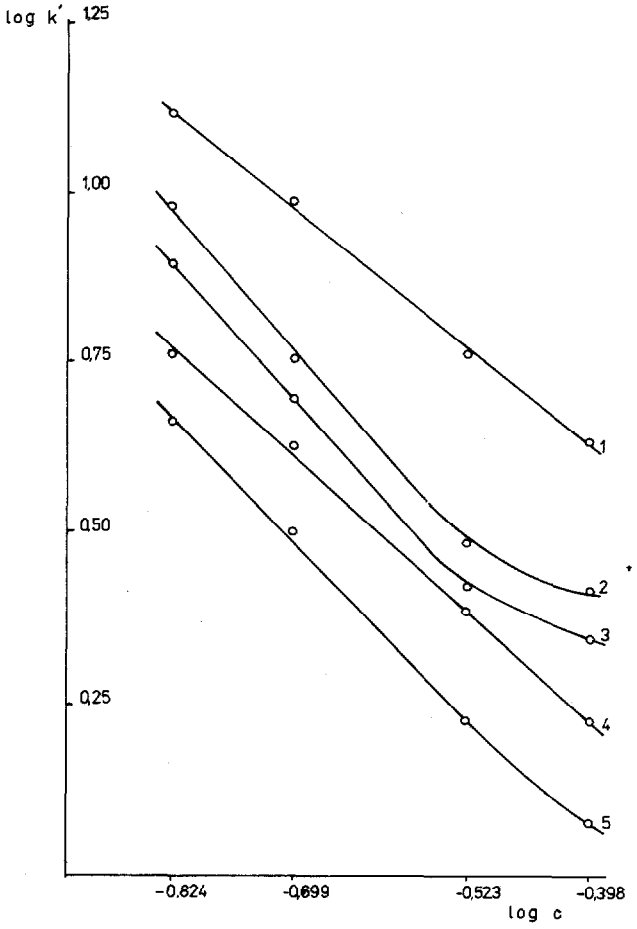


Fig. 1. Plots of retention *vs.* mobile phase composition for some substituted phenylureas on Silasorb S (10 μm, 300 mm × 4.2 mm I.D.). *k'* = Capacity factor; *c* = % (v/v) of *n*-propanol in *n*-hexane as the mobile phase. Compounds: 1 = fenuron; 2 = N'-4-methyl-3-chlorophenyl-N-methylurea; 3 = monuron; 4 = chlortoluron; 5 = diuron.

TABLE III

RETENTION VOLUMES, V_R, AND CAPACITY FACTORS, k', OF SUBSTITUTED PHENYLUREAS AND PHENYLUREA HERBICIDES ON SILASORB DEA IN NON-AQUEOUS MOBILE PHASES

I = 5% *n*-Propanol in *n*-hexane; II = 10% *n*-propanol in *n*-hexane; III = 15% *n*-propanol in *n*-hexane; IV = 20% *n*-propanol in *n*-hexane; V = 30% *n*-propanol in *n*-hexane.

Compound	*I*		*II*		*III*		*IV*		*V*	
	V_R (cm^3)	k'	V_R (cm^3)	k'	V_R (cm^3)	k'	V_R (cm^3)	k'	V_R (cm^3)	k'
Fenuron	28.45	11.12	12.67	4.90	8.52	2.63	6.31	1.69	4.20	0.79
Desfenuron	–	–	43.50	17.54	24.39	9.40	16.47	6.02	9.18	2.91
Monuron	29.77	11.69	12.11	4.20	7.38	2.14	5.85	1.49	–	–
Diuron	30.64	12.06	12.64	4.39	8.59	2.66	6.41	1.73	–	–
Chlortoluron	22.76	8.70	10.31	3.39	7.02	1.99	5.49	1.34	–	–
N′-4-Methyl-3-chlorophenyl-N-methylurea	–	–	36.91	14.73	19.75	7.42	12.60	4.37	8.05	2.43
Metoxuron	–	–	21.41	8.13	13.41	4.71	8.83	2.76	5.72	1.44
Deschlormetoxuron	–	–	29.50	11.57	10.87	3.63	7.20	2.07	4.85	1.07
Isoproturon	15.33	5.53	7.24	2.09	5.41	1.31	4.20	0.79	–	–
Fluometuron	20.31	7.66	9.22	2.93	6.32	1.69	5.12	1.18	–	–
Neburon	14.93	5.36	7.27	2.10	5.46	1.32	4.23	0.80	–	–
Monolinuron	9.28	2.95	6.27	1.67	4.88	1.08	4.06	0.73	–	–
Linuron	11.67	3.97	6.78	1.89	5.46	1.33	4.27	0.82	–	–
Metobromuron	9.42	3.01	6.99	1.98	5.03	1.14	4.18	0.08	–	–
Chlorbromuron	12.37	4.27	9.71	3.14	5.41	1.31	4.39	0.87	–	–
N,N′-Bis(3-chloro-4-methylphenyl)urea	–	–	58.34	23.86	32.14	12.70	18.92	7.07	11.92	4.08
N-Phenylurea	–	–	88.06	36.54	48.08	19.50	30.17	11.86	18.28	6.79
N,N-Diethyl-N′-phenylurea	14.76	5.29	7.95	2.39	5.54	1.36	4.39	0.87	–	–
N-Phenyl-N′-isopropylurea	–	–	20.32	7.66	11.51	3.91	8.08	2.44	–	–
N-*n*-Butyl-N′-phenylurea	–	–	19.97	7.51	11.21	3.78	7.81	2.33	–	–
N-*sec.*-Butyl-N′-phenylurea	–	–	18.32	6.81	10.38	3.43	7.21	2.07	–	–
N-Isobutyl-N′-phenylurea	51.23	20.83	19.90	7.48	11.39	3.86	7.84	2.34	–	–
N-Methoxy-N-methyl-N′-phenylurea	7.37	2.14	5.63	1.40	4.78	1.04	4.03	0.72	–	–
N-Benzyl-N′-phenylurea	–	–	45.69	18.48	23.25	8.91	14.91	5.35	8.56	2.65

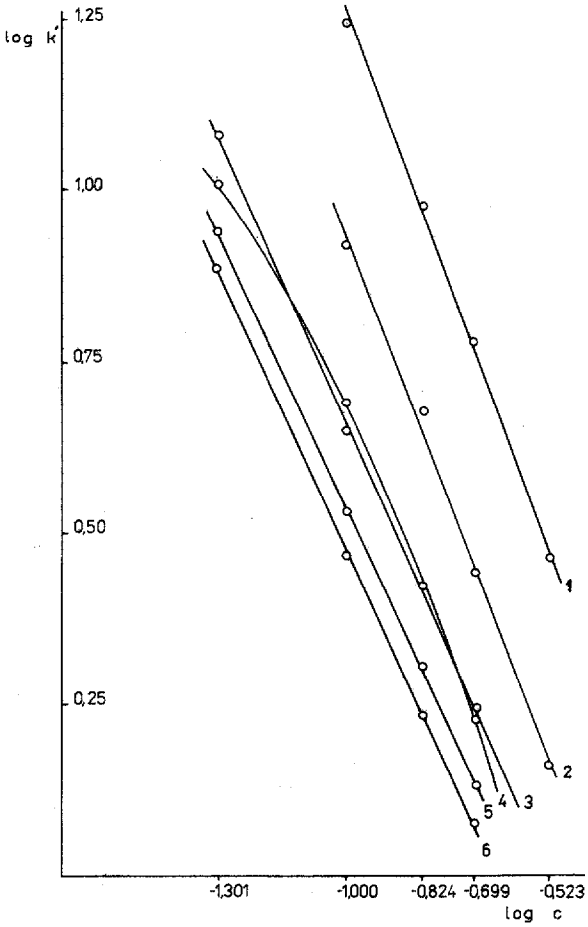


Fig. 2. Plots of retention *vs.* mobile phase composition for some substituted phenylureas on Silasorb DEA (15 μm, 300 mm × 3.8 mm I.D.). Compounds: 1 = desfenuron; 2 = metoxuron; 3 = diuron; 4 = fenuron; 5 = chlortoluron; 6 = fluometuron. Other details as in Fig. 1.

chromatography on unmodified silica gel and on the other bonded polar stationary phases, such as amino- or cyanopropylsilicas[43–50], and indicates the predominance of the competition adsorption mechanism for phenylurea herbicides on the ion exchangers tested.

Significant deviations from linearity occur for the Silasorb S column in the mobile phases containing 30–40% of *n*-propanol. Even increasing retention with increasing concentration of *n*-propanol in the mobile phase is observed for some compounds in this region (Table II). Similar minima in plots of the retention *vs.* mobile phase composition were observed in our earlier experiments with unmodified and modified Spheron gels[40–42] at certain methanol concentrations in methanol–water mobile phases. These minima have been attributed to the change from a reversed-phase to a normal-phase mechanism. It is expected that the composition of the mobile phase where the lipophilic contribution to retention becomes more significant than

the polar contribution depends on the nature of the column packing material, on the components of the mobile phase and on the structures of the solute molecules. Consequently, it is possible that this change between the normal-phase and non-aqueous reversed-phase mechanisms occurs at approximately 40% of *n*-propanol in *n*-hexane for Silasorb S and some substituted phenylureas and phenylurea herbicides.

Influence of the structures of the solute molecules on retention. The retention of substituted phenylureas on Silasorb S decreases significantly with increasing substitution of the urea nitrogen, especially with a methoxy group (Table II). The decrease in retention is relatively more significant with increasing length of the alkyl substituents on the urea nitrogen. Consequently, the most strongly retained compound is non-substituted phenylurea. Fenuron is retained less strongly than desfenuron, chlortoluron less strongly than N′-4-methyl-3-chlorophenyl-N-methylurea and neburon less strongly than diuron. Chlorbromuron, metobromuron, monolinuron and linuron with N-methoxy substituents are the least strongly retained compounds of all the phenylureas tested.

Methoxy substituents on the benzene ring of substituted phenylureas significantly increase the retention, whereas halogeno and alkyl substituents decrease the retention in proportion to the increasing size and number of the substituents. Thus the elution order fluometuron, diuron, chlortoluron, monuron and isoproturon is determined by the substituents on the benzene ring: CF_3, 2 Cl, Me + Cl, Cl and isopropyl.

The influence of the substituents on the urea nitrogens on the retention of substituted phenylureas on the anion exchanger Silasorb DEA is similar to the behaviour observed on Silasorb S (Table III). This means that the phenylurea herbicides with methoxy substituents on the urea nitrogen are the least strongly retained of all the compounds tested (monolinuron, linuron, metobromuron, chlorbromuron and N-methoxy-N-methyl-N′-phenylurea); non-substituted phenylurea is retained more strongly than other compounds, neburon is retained less strongly than diuron, fenuron less strongly than desfenuron and chlortoluron less strongly than N-4-methyl-3-chlorophenyl-N-methylurea.

The substitution of the benzene ring of phenylureas with a methoxy group significantly increases the retention on Silasorb DEA (fenuron, deschlormetoxuron), whereas substitution with an alkyl group decreases the retention (fenuron, isoproturon). Substitution of the benzene ring with one or more halogeno substituents may result in a decrease or in an increase in retention of phenylurea herbicides, depending on the number and position of the halogen atoms and of other substituents, and the order of elution (relative retention) depends also on the mobile phase composition. This behaviour differs from the structural dependence of the retention of the phenylurea herbicides on Silasorb S cation exchanger.

Comparison of the selectivity of various adsorbents

The retentions (separation factors) of phenylurea herbicides and other substituted phenylureas, relative to fenuron as the standard compound, are compared in Table IV for unmodified silica gel and various chemically bonded materials. The values are slightly higher on Silasorb 300 than on Silasorb Nitrile for most compounds tested, except for N′-phenyl-N-monoalkylureas, N′-phenyl-N-methoxy-N-alkylureas and for N′-phenyl-N-dialkylureas with longer alkyl chains. The relative

TABLE IV

SELECTIVITY COEFFICIENTS (RELATIVE RETENTIONS WITH RESPECT TO FENURON), $r_{is} = k'$ (compound)/k'(fenuron), OF PHENYLUREA PESTICIDES AND OTHER SUBSTITUTED PHENYLUREAS ON VARIOUS ADSORBENTS IN MOBILE PHASES CONTAINING VARIOUS AMOUNTS OF *n*-PROPANOL (c = %, v/v) IN *n*-HEXANE

Compound	c	r_{is}				
		Silasorb S	*Silasorb DEA*	*Silasorb Amine*	*Silasorb Nitrile*	*Silasorb 300*
Desfenuron	5	–	–	2.06	1.02	0.85
	10	–	3.58	2.01	0.89	0.76
	15	–	3.56	–	–	0.73
	20	–	3.56	1.54	–	–
Monuron	5	–	1.05	0.93	0.84	1.11
	10	–	–	0.97	0.81	1.11
	15	0.60	0.82	–	–	1.11
	20	0.51	0.88	0.94	–	–
Diuron	5	–	1.08	0.80	0.69	0.91
	10	–	1.08	0.84	0.70	0.87
	15	0.35	1.01	–	–	0.87
	20	0.33	1.02	0.90	–	–
Chlortoluron	5	–	0.78	0.67	0.72	0.78
	10	–	0.69	0.73	0.71	0.78
	15	0.43	0.76	–	–	0.78
	20	0.44	0.79	0.76	–	–
N'-4-Methyl-3-chloro-	5	–	–	1.68	0.72	0.70
phenyl-N-methylurea	10	–	3.01	1.57	0.66	0.63
	15	0.73	2.82	–	–	0.61
	20	0.58	2.58	1.53	–	–
Metoxuron	5	–	–	1.57	1.49	1.70
	10	–	1.66	1.56	1.36	1.56
	15	–	1.79	–	–	1.47
	20	1.28	1.64	1.42	–	–
Deschlormetoxuron	5	–	–	1.48	1.58	1.77
	10	–	2.36	1.56	1.46	1.61
	15	–	1.38	–	–	1.55
	20	3.99	1.22	1.36	–	–
Isoproturon	5	–	0.50	0.61	0.75	0.83
	10	–	0.43	0.67	0.72	0.86
	15	0.67	0.50	–	–	0.85
	20	0.53	0.47	0.71	–	–
Fluometuron	5	–	0.69	0.62	0.62	0.75
	10	–	0.60	0.67	0.62	0.76
	15	0.28	0.64	–	–	0.74
	20	0.24	0.70	0.73	–	–
Neburon	5	–	0.48	0.23	0.44	0.12
	10	–	0.43	0.33	0.48	0.13
	15	0.12	0.50	–	–	–
	20	0.10	0.47	0.34	–	–

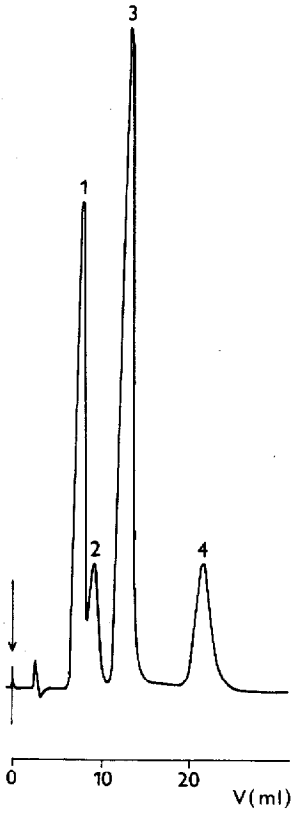
(*Continued on p. 164*)

TABLE IV (*continued*)

Compound	*c*	r_{is}				
		Silasorb S	*Silasorb DEA*	*Silasorb Amine*	*Silasorb Nitrile*	*Silasorb 300*
Monolinuron	5	–	0.26	0.20	0.41	0.19
	10	–	0.34	0.33	0.56	0.30
	15	0.08	0.41	–	–	–
	20	0.08	0.43	0.49	–	–
Linuron	5	–	0.36	0.23	0.43	0.21
	10	–	0.38	0.37	0.56	0.30
	15	0.08	0.50	–	–	–
	20	0.07	0.48	0.43	–	–
Metobromuron	5	–	0.27	0.20	0.40	0.19
	10	–	0.40	0.35	0.56	0.30
	15	0.08	0.43	–	–	–
	20	0.08	–	0.48	–	–
Chlorbromuron	5	–	0.38	0.23	0.33	0.20
	10	–	0.64	0.39	0.57	0.29
	15	0.08	0.50	–	–	–
	20	0.08	0.52	0.44	–	–
N,N′-Bis(3-chloro-4-methylphenyl)urea	5	–	–	0.63	0.38	0.03
	10	–	4.87	0.71	0.40	0.04
	15	0.25	4.83	–	–	–
	20	0.21	4.18	0.78	–	–
N-Phenylurea	5	–	–		1.48	–
	10	–	7.46		1.20	1.11
	15	–	7.41		–	–
	20	–	7.02		–	–
N,N-Diethyl-N′-phenylurea	5	–	0.48		0.66	–
	10	–	0.49		0.71	0.26
	15	0.42	0.52		–	–
	20	0.33	0.52		–	–
N-Phenyl-N′-isopropylurea	5	–	–		0.60	–
	10	–	1.56		0.59	0.16
	15	0.48	1.49		–	–
	20	0.35	1.45		–	–
N-*n*-Butyl-N′-phenylurea	5	–	–		0.56	–
	10	–	1.53		0.55	0.11
	15	0.45	1.44		–	–
	20	0.42	1.38		–	–
N-*sec*.-butyl-N′-phenylurea	5	–	–		0.55	–
	10	–	1.39		0.55	0.10
	15	0.38	1.30		–	–
	20	–	1.23		–	–
N-Isobutyl-N′-phenylurea	5	–	1.87		0.54	–
	10	–	1.53		0.54	0.10
	15	0.38	1.47		–	–
	20	0.37	1.39		–	–

TABLE IV (*continued*)

Compound	*c*	r_{is}				
		Silasorb S	*Silasorb DEA*	*Silasorb Amine*	*Silasorb Nitrile*	*Silasorb 300*
N-Methoxy-N-methyl-N'-phenylurea	5	–	0.19		0.36	–
	10	–	0.29		0.52	0.25
	15	0.06	0.39		–	–
	20	0.07	0.47		–	–
N-Benzyl-N'-phenylurea	5	–	–		0.77	–
	10	–	3.77		0.74	0.12
	15	0.37	3.39		–	–
	20	0.27	3.17		–	–



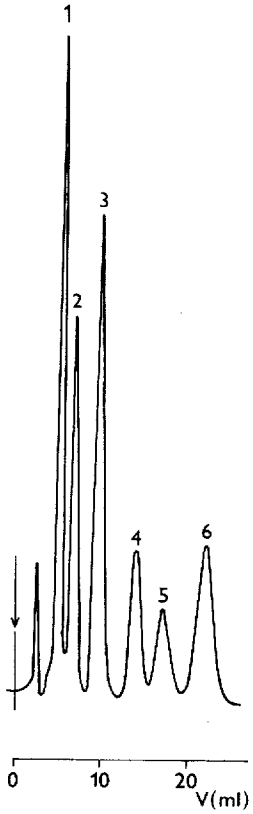


Fig. 3. Separation of phenylurea herbicides on Silasorb DEA column (15 μm, 300 mm × 3.8 mm I.D.) using 10% (v/v) *n*-propanol in *n*-hexane as the mobile phase. Flow-rate: 2 cm^3 min^{-1}. Detection: UV, 254 nm. Compounds: 1 = neburon; 2 = fluometuron; 3 = monuron; 4 = metoxuron.

Fig. 4. Separation of phenylurea herbicides and other substituted phenylureas on Silasorb DEA (15 μm, 300 mm × 3.8 mm I.D.) using 20% (v/v) *n*-propanol in *n*-hexane as the mobile phase. Flow-rate: 2 cm^3 min^{-1}. Detection: UV, 254 nm. Compounds: 1 = chlorbromuron; 2 = fenuron; 3 = metoxuron; 4 = N'-4-methyl-3-chlorophenyl-N-methylurea; 5 = desfenuron; 6 = N,N'-bis(3-chloro-4-methylphenyl)urea.

retentions of N′-phenyl-N-monoalkylureas are significantly higher on Silasorb Amine than on Silasorb Nitrile, and higher on Silasorb DEA than on Silasorb Amine. The values of most N′-phenyl-N,N-dialkylureas on Silasorb DEA are close to those on Silasorb 300.

A methoxy substituent on the urea nitrogen decreases strongly both the absolute and the relative retentions on Silasorb S in comparison to other adsorbents, whereas a methoxy substituent on the benzene ring of phenylureas increases and an halogen substituent decreases the relative retentions. The length of the alkyl substituents in phenylurea herbicides has only a small influence on their relative retentions on Silasorb S, but the differences in selectivities (relative retentions) of phenylureas differing in the number and positions of other substituents are more significant than on other packing materials tested.

These differences may be utilized for separations of some phenylurea herbicides. Figs. 3 and 4 show two examples of such separations on a Silasorb DEA column. The increased selectivity of Silasorb S for the individual phenylurea herbicides makes it possible to accomplish better separations of certain solutes than on other adsorbents. For example, desfenuron, diuron, fluometuron and chlortoluron can be separated in mobile phases containing 20–30% *n*-propanol in *n*-hexane on

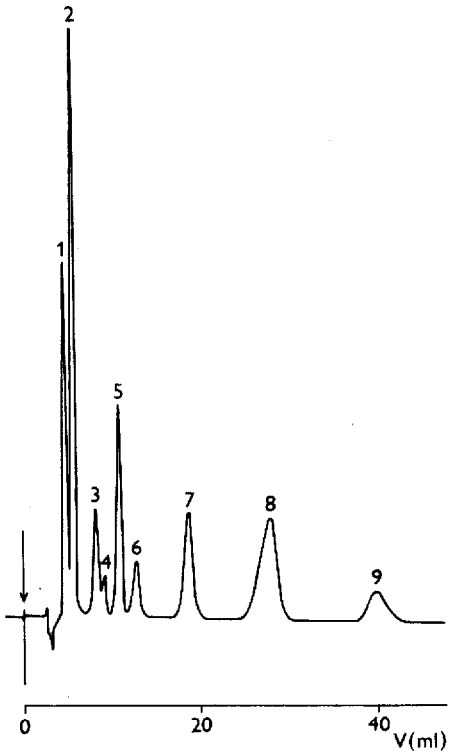


Fig. 5. Separation of phenylurea herbicides on Silasorb S (10 μm, 300 mm × 4.2 mm I.D.) using 20% (v/v) *n*-propanol in *n*-hexane as the mobile phase. Flow-rate: 2 cm^3 min^{-1}; detection UV, 254 nm. Compounds: 1 = linuron; 2 = neburon; 3 = N,N′-bis(3-chloro-4-methylphenyl)urea; 4 = fluometuron; 5 = diuron; 6 = chlortoluron; 7 = isoproturon; 8 = fenuron; 9 = desfenuron.

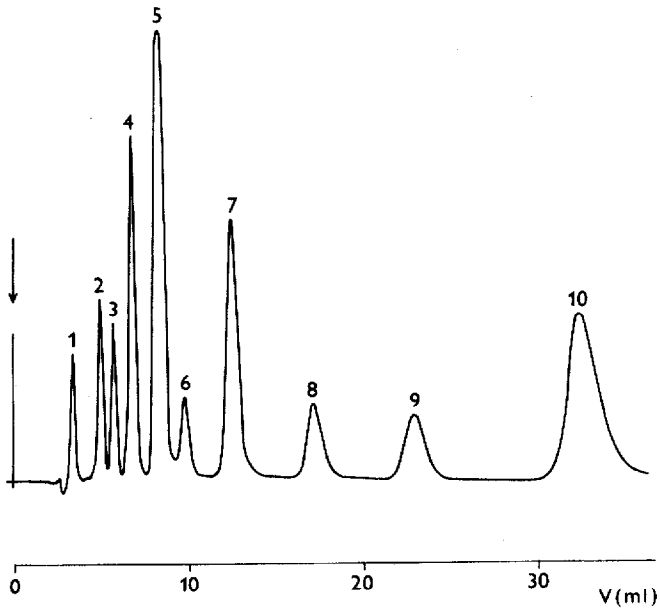


Fig. 6. Separation of phenylurea herbicides on Silasorb S (10 μm, 300 mm × 4.2 mm I.D.) using 40% (v/v) *n*-propanol in *n*-hexane as the mobile phase. Flow-rate: 1 cm^3 min^{-1}. Detection: UV, 254 nm. Compounds: 1 = linuron; 2 = N,N'-bis(3-chloro-4-methylphenyl)urea; 3 = diuron; 4 = chlortoluron; 5 = monuron; 6 = isoproturon; 7 = fenuron; 8 = desfenuron; 9 = hydroxymetoxuron; 10 = deschlormetoxuron.

Silasorb S (Figs. 5 and 6), whereas such a separation would not be feasible on columns packed with other materials.

CONCLUSIONS

Silasorb column packing materials with various chemically bonded groups having medium or strong polarities can be used for chromatography of various substituted phenylureas, including phenylurea herbicides in non-aqueous mobile phases. In these systems, the bonded groups including the ion-exchange functional groups behave as the adsorption centres that display more or less specific interactions with the chromatographed compounds. The differences in these interactions for various phenylurea herbicides may be utilized for their chromatographic separations on Silasorb ion exchangers in non-aqueous systems. The absolute retention of phenylurea herbicides generally increases with increasing polarity of the bonded phases and is especially strong on the cation exchangers, so that the order of retention of most compounds for a given constant composition of the *n*-propanol–*n*-hexane mobile phase is as follows: Silasorb Nitrile < Silasorb 300 < Silasorb Amine < Silasorb DEA < Silasorb S. The structural influences on the retention of phenylurea herbicides on the packing materials studied suggest that proton-donor and proton-acceptor interactions are most important in controlling the retention on Silasorb DEA and Silasorb S ion exchangers in non-aqueous mobile phases, but dipole–dipole interactions also contribute.

Reversed-phase chromatography on octadecylsilica or on octylsilica columns provides better selectivities for separations of phenylurea herbicides differing only in the lengths of the alkyl substituents, but non-aqueous chromatography on the cation exchanger Silasorb S offers a valuable complementary method for separation of these compounds. For example, the separation of certain pairs of phenylurea herbicides, such as desfenuron/deschlormetoxuron, deschlormetoxuron/fenuron, monolinuron/fluometuron and metobromuron/isoproturon, which is difficult in reversed-phase systems, can easily be achieved on Silasorb S in *n*-hexane–*n*-propanol mobile phases (see, for example, the separation of desfenuron, deschlormetoxuron and fenuron in Fig. 6).

It is expected that chemically bonded cation or anion exchangers will prove useful also for separations of other types of neutral non-ionic compounds.

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