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USE OF THE CONCEPT OF GAS CHROMATOGRAPHIC SELECTIVITY IN THE CHOICE OF PREFERRED STATIONARY PHASES

L. V. SEMENCHENKO*

A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR, Kazan (U.S.S.R.)

and

M. S. VIGDERGAUZ

Grozny Scientific Research Institute for Petroleum Refining, Grozny (U.S.S.R.)

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SUMMARY

Stationary phases used in gas chromatography belong to seven types according to the sequence of five polarity factors, Φ (arranged according to their order of magnitude). The combined relationship $y - z = f_1(x)$ and $y - z = f_2(s - u)$, where each of the types has separate characteristic regions, represents the principal quantitative regularities of the classification suggested. The use of the relationship $(\Phi - x) = f_3(x)$ when choosing a preferred stationary phase provides a set of stationary phases with extreme values of polarity factors and also stationary phases with their original combinations, which cannot be substituted by binary phases. The results are compared with those for sets of preferred stationary phases selected on the basis of their chemical composition and their frequency of citation in the literature.

INTRODUCTION

The term "preferred stationary phases" (PSPs)¹⁻⁵ implies the construction of hierarchical pyramids of the stationary phases used in practice. The lists of recommended PSPs with stepwise extensions (see, e.g., ref. 6) make it possible to take into account the variety of types of analytical problems encountered and to accumulate detailed information concerning PSPs. The most representative sets of the PSPs are composed on the basis of the classification of the stationary phases according to their chemical composition⁷ or to the Rohrschneider and McReynolds polarity factors⁸⁻¹⁰. In the latter instance the stationary phases can be chosen as preferred ones with extreme values of the factors^{11,12} or their differences⁴ which cannot be substituted by binary phases. There are no major differences between the results obtained by employing different methods, including the formation of sets of stationary phases taking into account the frequency of their exploitation¹ and a definite polarity interval¹³. However the sets obtained as stated above contain about 12-15 PSPs with a conventional (not rigorously substantiated) hierarchy and depend on their initial data. More-

over, there are no PSPs with hydroxyl selectivity (the maximum value of the factor difference being $y - z$) as recommended elsewhere^{5,11}, as evidenced by the insufficient systematization of the extensive set of 5–10 polarity factor values when taking into account only one of the characteristics, *viz.*, the proximity of the numerical values of the factors¹⁰, an increase in one of the constants¹⁴ or the chemical constitution of stationary phases¹⁵.

The object of this paper is the classification of differences between the five most informative polarity factors of stationary phases. The intervals of selectivity of the separation of different classes of substances are limited⁴ by extreme values of the corresponding factors. Such relationships require an extensive number of tabulated data^{10,14–16} on the basis of a simple and obvious method.




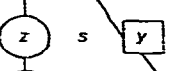
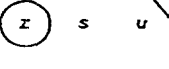
THEORETICAL

The numerical values of polarity factors (Φ) are expressed as differences in retention indices (ΔI) of standard substances on columns containing the stationary phase under investigation, and with squalane in the case of logarithmic indices $\Phi = 0.01 \Delta I$ and in the case of linear analogues $\Phi = \Delta J$. For greater reliability the results obtained are presented in both symbolic and graphical forms.

The symbolic form presents any stationary phase as a sequence of five Rohrschneider factors (x, y, z, u and s) in order of increasing values. The set of common stationary phases has the same sequence for all of the factors. The widely employed stationary phases belong to seven types owing to the above rule (see Table I). For all of these stationary phases the factor x is smaller than the other factors and

TABLE I

CLASSIFICATION OF STATIONARY PHASES ON THE BASIS OF ROHRSCHEIDER FACTORS

Type of stationary phase	x	Order of increasing polarity factors	PSP	Chemical characteristics of the stationary phases	Invariants				
					$\frac{y-z}{x}$	$\frac{y}{x}$	$\frac{z}{x}$	$\frac{u}{x}$	$\frac{s}{x}$
I	0.32	$\Phi_i < 1.50$	Apiezon L (Squalane)	Hydrocarbons and methyl silicones					
II	1.41		QF-1	Trifluorosilicones	-0.7	1.6	2.4	2.9	2.1
III	1.75		Polyphenyl ether (5 rings)	PPE, phenyl silicones, silicones of intermediate polarity	-0.1	1.4	1.5	2.2	1.7
IV	6.00		1,2,3-Tris(β -cyanoethoxy)propane	Nitriles, nitrile silicones, polyesters	0.2	1.5	1.3	2.0	1.7
V	3.22		PEG 20M	PEG, esters and ethers	0.4	1.8	1.4	2.3	1.7
VI	0.71		Tri(ethylhexyl)phosphate	Phosphates	1.3	2.8	1.4	2.3	1.8
VII	3.71	$(s - u) > 0; (> 1.0)$	Diglycerol	Polyalcohols, water, acidic substances					

therefore its numerical value is specified. Most widely employed stationary phases are connected with five types of symbols (II–VI), when the factors y and z are displaced as regards one another and also the factors x , s and u . Stationary phases of low polarity (type I) have $\Phi < 1.50$. Stationary phases of type VII have a positive difference of factors $s - u$ owing to the inversion of the order of the values of the factors x , u and s . Phases of the above type also have at least one of the values of $\Phi < 1.50$.

As a majority of extreme values of Φ and $\Delta\Phi$ are interrelated⁴, three characteristics have been chosen as conventionally independent ones, x , $y - z$ and $s - u$, as the first stage of choosing the PSPs. The principal features of the symbolic systematization of factors are in this case expressed by a combined plot (see Fig. 1):

$$y - z = f_1(x) \tag{1}$$

$$y - z = f_2(s - u)$$

On the above plot the stationary phases of each type have specific regions, the boundaries between them being mainly defined by the term $(y - z)/x$.

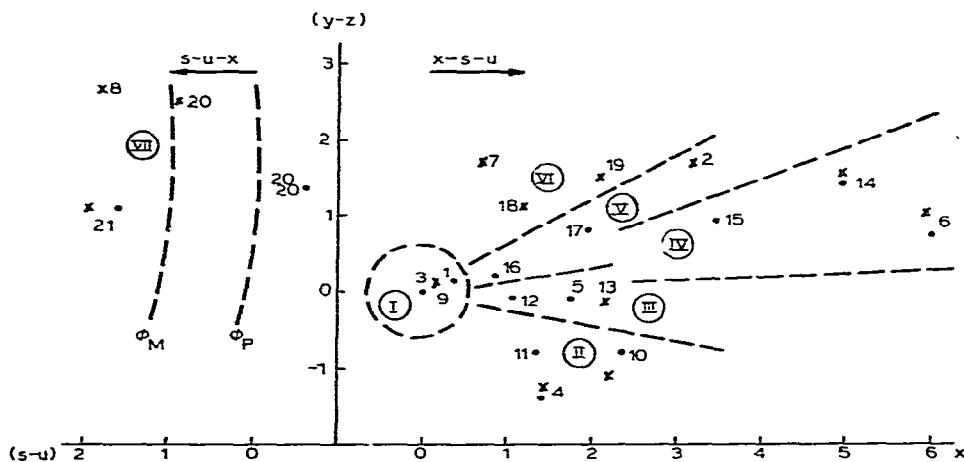


Fig. 1. Characteristic areas of the seven types of stationary phases. The numbers of the types of stationary phases correspond to Table I and the numbers of the PSPs to Table II. ●, Rohrschneider factors (Φ_R); ×, McReynolds factors (Φ_M). The arrows indicate the order increase in the factors x , u and s .

The selectivity of the separation of a complex mixture depends both on the values of Φ and $\Delta\Phi$ and also on the terms Φ/x and $\Delta\Phi/x$ (ref. 17).

When Φ and $\Delta\Phi$ are equal for two stationary phases, the one with the smaller factor x is more selective because in this instance it is possible to separate the investigated class of solutes not only from one another but also from many accompanying concomitant classes of solutes. In a general case of analysis of complex mixtures, the selectivity of stationary phases depends on the combination of the values of x and Φ/x . The values of Φ/x and also the relationship $\Phi - x = f_3(x)$ plotted in Fig. 2 are used for finding stationary phases with an optimal combination of polarity factors.

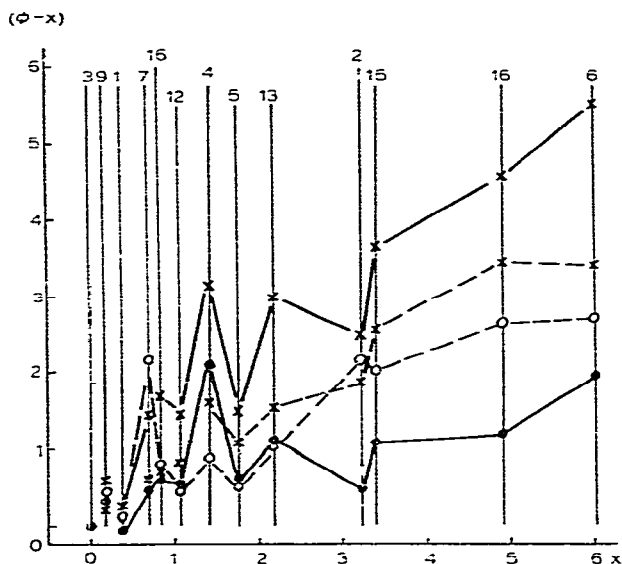


Fig. 2. Extremes of the retention spectra of PSPs of types III and V and others irreproducible by binary sorbents. The numbers of the PSPs correspond to Table II.

The graphs in Figs. 1 and 2 were plotted on the basis of the Rohrschneider factors¹⁶ but when there were none the McReynolds factors¹⁰ were used.

The approximate values of the invariants of the stationary phases of types II-VI are given in Table I.

RESULTS AND DISCUSSION

The stationary phases are listed in Table I on the basis of the Rohrschneider factors¹⁶. The use of the corresponding McReynolds data^{10,14,15} gives a similar distribution of the stationary phases of types I to VI. Some stationary phases migrate to other neighbouring types, *e.g.*, nitrile silicone OV-275 migrates from type IV to type V. Fig. 1 allows one to eliminate some insignificant divergences that occur in the correlations between the chemical constitution and selectivity characteristics.

The factor difference $s - u$ singles out mainly stationary phases of type VII with acidic properties and the "sieve effect". When McReynolds factors are used the boundary of type VII on the plot of the relationship $y - z = f_2(s - u)$ is removed by about 100 Kováts retention index units because the value of u/x is diminished. The invariant s/x is virtually invariable for the stationary phases of this boundary zone (Hyprose SP-80, FFAP, Quadrol, etc.). The deviations from the additivity of retention values are characteristic of the above intermediate group of stationary phases but to a lesser extent than those of diglycerol and other stationary phases of type VII. With diglycerol and related stationary phases with molecules saturated with hydroxylic groups the inversion of the order of elution of polar solute homologues occurs.

Stationary phases of types I, II, IV and VI have extreme values of x and $y - z$. The value $(y - z)/x \approx 0.4$ corresponds to the boundary between the types V, VI and

II, III, IV that selectively retain OH and CO groups correspondingly. Trifluorosilicones are the most widely used stationary phases with extreme carbonyl-carboxylic selectivity. 1-Alkanols elute earlier than 2-alkanones with the same carbon number on columns containing QF-1 and related stationary phases, in spite of the fact that the boiling points of the former are higher than those of the latter. Moreover, the extreme carbonyl selectivity (with respect to hydroxylic groups) is a unique property of the stationary phases of type II. At the same time, the opposite extreme (the selective retention of molecules with OH groups) may be reached with stationary phases of types VI and IV. In the latter instance the high selectivity is due to the polarity of stationary phases (high values of factor x).

As has been pointed earlier¹⁸, the extreme values of the sorption capacity (measured in terms of absolute retention) are related to stationary phases of types III and IV. Nevertheless, corresponding experiments (which are important, *e.g.*, in minimizing the time of separation) showed that extremes of the relative retention of neighbouring homologues¹⁸, some $\Delta\Phi$ values⁴, etc., also occur. The above rule is obvious on the plot of $\Phi - x = f_3(x)$, where stationary phases of types III and V give many extremes that cannot be obtained by the method of binary phases^{19,20} on the basis of stationary phases of other types. Stationary phases of types III and IV have low values of all of the invariants Φ/x (Table I) owing to the selective retention of benzene.

Binary sorbents based on PSPs with extreme values of Φ or $\Delta\Phi$ and also with any other extreme absolute or relative retention values of solutes enable one to obtain selectively values not only of all the stationary phases used but also of those not yet synthesized. Therefore seven stationary phases (one from each type) form the minimum set of PSPs. The optimal set of PSPs listed in Table II includes three stationary phases of each type with the original combinations of Φ/x values. Such a set gives the possibility of reproducing precisely the selectivity characteristics of almost any stationary phase and also to extend the selectivity extremes to wider limits of the factor x .

The distribution of the types of stationary phases and of the individual stationary phases in the optimal set has been carried out, taking into account the relationship $\Phi - x = f_3(x)$. The values of Φ for stationary phases of types I, III, IV and V¹⁸ are connected by the linear relationship

$$\Phi = \Phi_{\max} P_{\sigma} \quad (2)$$

where P_{σ} is the statistical polarity of the stationary phase, in this case defined as

$$P_{\sigma} = \frac{1}{3} (x + y + z)$$

Considerable systematic deviations from linearity are observed with stationary phases of types II, VI and VII. However, the numerical values of Φ and $\Delta\Phi$ are also linearly connected within one type, which is due to the same order of the factors of the stationary phases. The above values may be calculated approximately on the basis of factor x as a function of the conventional polarity (P_i):

$$\frac{x_i}{x_{\text{PSP}}} = \frac{\Phi_i}{\Phi_{\text{PSP}}} = \frac{\Delta\Phi_i}{\Delta\Phi_{\text{PSP}}} = P_i \quad (3)$$

TABLE II
PSPs AND THEIR SELECTIVITY CHARACTERISTICS

No.	PSP	Type	x	Invariants				
				$\frac{y-z}{x}$	$\frac{y}{x}$	$\frac{z}{x}$	$\frac{u}{v}$	$\frac{s}{x}$
<i>PSPs of different polarity:</i>								
1	Apiezon L (Squalane)	I	0.32	0.44	1.22	0.78	1.50	1.66
2	PEG 20M (or PEG 4000)	V	3.22	0.52	1.66	1.14	1.78	1.58
<i>PSPs with extreme selectivity characteristics:</i>								
3	Squalane	I	0	0	0	0	0	0
4	QF-1 (or SKTFT-100)	II	1.41	-1.00	1.51	2.52	3.36	2.16
5	PPE (5 rings) [or PPE (6 rings)]	III	1.75	-0.04	1.30	1.34	1.86	1.62
6	1,2,3-Tris(β -cyanoethoxy)propane	IV	6.00	0.13	1.45	1.32	1.92	1.57
7	Tri(ethylhexyl) phosphate	VI	0.71	2.41	4.06	1.65	3.03	1.86
8	Diglycerol	VII	3.71	0.72	2.23	1.51	1.82	2.30
<i>PSPs with original combinations of polarity factors:</i>								
9	SE-30	I	0.15	0.69	3.44	2.75	4.06	2.63
10	Zonyl E-7	II	2.23	-0.49	1.61	2.10	2.46	2.08
11	Zonyl E-91	II	1.34	-0.59	1.93	2.52	3.00	2.22
12	DC-710	III	1.05	-0.09	1.43	1.53	2.39	1.81
13	OV-225	III	2.17	-0.06	1.47	1.54	2.38	1.70
14	Diethylene glycol succinate	IV	4.93	0.29	1.53	1.25	1.93	1.70
15	Polyethylene glycol adipate	IV	3.43	0.27	1.60	1.32	2.08	1.75
16	Diisodecyl phthalate	V	0.38	0.26	1.99	1.72	3.04	1.86
17	Polypropylene glycol sebacate	V	1.93	0.41	1.75	1.34	2.26	1.70
18	Ucon LB-550-X	VI	1.18	0.96	2.30	1.34	2.07	1.75
19	Polyglycol 15-200	VI	2.07	0.71	1.98	1.27	1.94	1.71
20	Hyprose SP-80	IV(VII)	2.96	0.46	1.88	1.43	2.20	1.99
21	Trimer acid	VII	0.89	1.24	3.07	1.85	2.32	4.14

where i refers to any stationary phase of the same type as the PSP, the differences $\Delta\Phi$ being calculated with regard for x . The deviations from linearity (eqn. 3) are not as great as with stationary phases of types II and VI (from eqn. 2). However, the values of the above deviations may be systematic (2-3 times the standard deviation).

According to eqns. 2 and 3, the increase in factor x (conventional polarity of the stationary phase) leads to an increase in other constants including many differences in the factors. This relationship is dominant and the abnormal values of some factors, being the basis of differentiation of the stationary phases into types I-VII, may be taken into account by introducing corrections δP_i to the polarity value, e.g.,

$$P_i = P_\sigma + \delta P_i$$

This is followed by a valid supposition that most separation problems may be solved by altering only the factor x and the two stationary phases of different polarities (with additive retention values of solutes) are dominant in the list of PSPs. They make it possible to achieve the group separation of solutes of different classes (selective or alternative elution of its homologues), and identification on the basis of retention values with a limited number of standards²¹⁻²³. The methods of predicting the reten-

tion values, e.g., the Rohrschneider constants⁸ is also based on the additive equations.

The retention characteristics of two PSPs of different polarity must provide on the one hand the possibility of controlling the factor x within wide limits, and on the other hand the stable resolution of numbers of various homologous series on binary sorbents and with two column retention plots^{2,4}. Apiezon L an polyethylene glycol 20M²⁵ possesses the above combination of properties, which is also confirmed by applying them in chromatographic identifications²¹⁻²³.

The list of PSPs given in Table II may be considered as the summit of the hierarchical pyramids of stationary phases applied in practice. The set of PSPs with the concept of selectivity as a basis is correlated with the results obtained by other methods, including statistics, and taking into account the chemical composition of molecules.

Systematization of the polarity factors of stationary phases may also be used for correlating the sets of standard substances used at various column temperatures^{9,10,26} and the results of the estimation of the selectivity of the constituents of the sets. The use of standard substances with other functional groups in the molecules involves mutual deviations of the characteristic areas on the plot (Fig. 1). For instance, as the value of the factor y is small for chloroform²⁶, a mutual displacement of the values $y - z$ occurs towards the negative region for all types of stationary phases.

The Rohrschneider factor system is a complex characteristic of stationary phases, as these factors contain information on the chemical structure of the molecules, on the relative and absolute retention values and their additivity. The stationary phases employed in practice have been distributed into seven types according to the order of increasing values of five Rohrschneider factors. The list of PSPs is made up to consist of three sections.

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