

CHROMSYMP. 100

SELECTIVE PHASES FOR WALL-COATED OPEN TUBULAR COLUMNS

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SUMMARY

Selectivity of gas chromatographic stationary phases is defined and discussed in terms of the types of interactions between solute molecules and the phase. A reexamination of previously published data gives insights into designing or choosing stationary phases for selectivity. Arguments are presented for the preference of silicone gum phases as well as the need for their careful characterization.

INTRODUCTION

Traditionally, the chromatographer has traded off column efficiency, selectivity and analysis time to achieve a desired separation. Though limited to low column plate numbers, the experimenter using packed gas chromatographic (GC) columns has achieved selectivity by choosing from an array of supports and stationary phases. The experimenter using capillary chromatography, accustomed to high column plate numbers but having fewer applicable stationary phases at his disposal, has relied on efficiency. As capillaries are increasingly applied to routine analysis, with its particular emphasis on productivity, there is an increased need for selective phases for faster analysis.

The purpose of this report is to present some considerations for designing and choosing selective phases for fused-silica wall-coated open tubular (FSWCOT) columns. Our guides will be the compilations of stationary phase data by McReynolds^{1,2} as well as some of the published work on "standard" or "preferred" phases, particularly that of Hawkes and co-workers^{3,4}. In analyzing these studies, which were concerned with packed column needs, we must bear in mind the general failure of the authors to consider the requirements of film and thermal stability for capillary columns. In a recent paper, Blomberg⁵ has reviewed new developments in stationary phases for capillary columns in considerable depth. This paper is not intended to review previous work exhaustively but rather to highlight significant correlations and contradictions in the hope of stimulating discussion of selectivity, polarity and the practical achievement of selective phases in routine analytical FSWCOT columns.

Because of the myriad separation problems facing the chromatographer, the definition of selectivity, in its broadest sense, has been left to the user. The resulting confusion has led to the use of over 200 phases in packed column GC, a trend that is starting to spread to capillary columns. Another consequence of this lack of defi-

nition is the synonymous use of the terms "selective" and "polar". For our purposes, we define selectivity as the interplay of the various types of interactions between solute and stationary phase, which include dispersion, dipole and acid-base as well as more specific types of complexation. The more traditional idea of selectivity meaning interaction with only one class of solute, is not generally applicable to the wide-ranging separations expected of FSWCOT columns. Polar phases possess chromatographic properties attributable primarily to the presence of permanent dipoles. In the case of silicones, these dipoles are due to the presence of heteroatoms in the organic functional groups. Using these definitions, all phases are selective; methyl and phenyl methyl silicones are non-polar and selective, but a 50% cyanopropyl silicone is polar and selective.

Various attempts have been made^{3,4,6,7} to produce a short list of well characterized phases covering a range of selectivities. The lack of well characterized selective polymers, combined with the desire to measure thermodynamic constants, frequently led to the inclusion of monomeric materials in these lists. Extremely limited temperature ranges and poor film building properties severely compromised the usefulness of many of these compounds for capillaries. Some of the authors have included silicones in their lists⁶; indeed, Grob⁸ recommended silicone gums for WCOT columns.

Now that modern polymer methods can produce silicone gums with a wide range of selectivities and well-characterized physical properties there is little need for the older phases. The many advantages of the new silicone gums include excellent film formation and stability plus enhanced ease of immobilization. Low glass transition temperatures⁹ and high thermal stability of the immobilized phases offer extended operating temperature ranges¹⁰. Furthermore they offer a wide choice of functional groups which can be varied in concentration, and possess unusually high diffusivities compared to other polymers^{11,12}. With the possible exception of the higher-molecular-weight polyethylene glycols, silicone gum stationary phases are the only reasonable choices for FSWCOT columns.

DISCUSSION

An excellent way to begin our discussion of selective phases is with the more fundamental interaction, dispersion. Methyl silicone, the most widely applied phase, interacts predominately through dispersion. Because of its wide applicability, methyl silicone is generally used as the basis for comparing stationary phase performance, especially for capillary columns.

The phenyl methyl silicones have found widespread application but have been subject to debate concerning their "polarity". Recently an exchange of letters took place concerning the polarity of phenyl-substituted silicones. The comments contained in these letters are indicative of the lack of understanding of the nature of these phases. One author considered a 50% phenyl methyl silicone to be "polar"; the reply attempted to address briefly the idea of selectivity vs. polarity and suggested the arbitrary definition of non-polar and polar in terms of McReynolds ΣAI . Let us now consider whether phenyl silicones are polar phases.

The data in Table I are quite instructive about phenyl phases and also show the difference between retention indices and retention volumes. Although retention

TABLE I

SELECTED RETENTION INDEX (I_x) AND SPECIFIC RETENTION VOLUME (V_g) DATA FOR METHYL SILICONE (SE-30), 25% PHENYL SILICONE (DG-550), AND 50% CYANOETHYL METHYL SILICONE (XF-1150)

Data obtained at 120°C¹

Compound	SE-30		DC-550		XF-1150	
	I_x	V_g	I_x	V_g	I_x	V_g
Hexane	—	11.9	—	10.0	—	3.2
Octane	—	40.1	—	36.4	—	7.5
Decane	—	133	—	127	—	19.6
Dodecane	—	422	—	429	—	51.2
Tetradecane	—	1319	—	1415	—	132
Hexadecane	—	3920	—	4400	—	335
Cyclohexane	677	19.1	699	19.0	753	6.1
Toluene	784	36.5	839	46.5	1072	27.8
Ethylbenzene	878	64.3	933	84.4	1166	43.5
<i>p</i> -Diethylbenzene	1068	197	1126	275	1344	101
Butanol	676	19.0	720	21.8	1113	33.9
3-Buten-1-ol	658	17.0	738	24.5	1131	36.8
<i>Meso</i> -2,3-Butanediol*	846	19.2	893	22.5	1582	61.0
3-Pentanone	693	21.1	753	26.9	1098	31.5
Ethyl propionate	700	22.0	757	27.7	1005	20.1

* All data at 140°C.

indices, I_x , can be quite useful as a guide to stationary phase selectivity and as a qualitative tool, they can be misleading since the absolute retention behavior of the reference hydrocarbons is ignored. Specific retention volume, V_g , the volume of carrier gas per gram of stationary phase required to elute a solute, is a direct consequence of the free energy of the solute-stationary phase interaction, and comparisons of V_g and I_x shifts (ΔI) are especially helpful. For instance, the high indices for aromatics on XF-1150 occur despite substantially lower V_g values compared to the other phases. Littlewood¹³ has pointed out that polar phases in general give reduced retention times, and it is only when dipolar or complexation interactions become predominant that increased V_g values are observed.

When compared to SE-30, the V_g values of the normal hydrocarbons on XF-1150 show the expected dramatic reduction in retention, whereas DC-550 (although giving a small decrease below decane) actually has an substantial retention increase above dodecane. The aromatics show increased I_x and V_g on DC-550 with an average ΔI of 56; the ΔI for XF-1150 averages 284 with substantially lower V_g . It is only with solutes having strong dipoles that XF-1150 gives both increased I_x and V_g . The *p*-diethylbenzene, ethylbenzene pair illustrate this behavior. ΔI for the pair is similar for SE-30 and DC-550 at 190 and 193 with both I_x and V_g increasing for the 25% phenyl phase. For XF-1150 the pair shows much higher values in I_x , reduced V_g and a decrease in ΔI . The hydroxyl containing solutes in Table I also show retention behavior for DC-550 which is more similar to SE-30 than XF-1150.

From the data above, one can see that the polarity of DC-550 is similar to that of SE-30 while XF-1150, with its CN dipoles, interacts in a substantially different

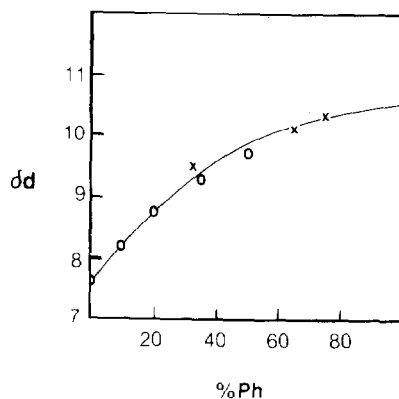
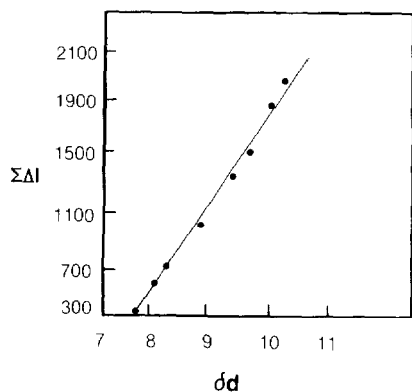


Fig. 1. Retention behavior (summation of McReynolds indices) of phenyl methyl silicones vs. Hildebrand solubility parameters.

Fig. 2. Solubility parameters vs. per cent phenyl (Ph) substitution in methyl silicones. Reprinted with permission from ref. 3. \circ , Viscosity less than 20 Stokes; \times , viscosity more than 500 Stokes.

fashion. The behavior of phenyl-substituted silicones is best explained by dispersion solubility similar to the methyl silicones. A plot (Fig. 1) of the summation ($\Sigma\Delta I$) of the McReynolds constants vs. the Hildebrand solubility parameters, δ_d , for a series of phenyl-substituted silicones indicates an excellent linear correlation. The solubility parameter does not correlate linearly with the amount of phenyl substitution (Fig. 2), thus giving even more credibility to a physical significance of the linear correlation with $\Sigma\Delta I$. The δ_d values are calculated from the indices of refraction of the phases. Since refraction of light is a consequence of bond polarizability, we may conclude that the primary mode of interaction of phenyl silicones is due to polarizability rather than the interaction of any permanent dipoles.

Preliminary results from our laboratory confirm this line of reasoning for phenyl phases. Columns prepared from an experimental cross-linked 50% phenyl methyl silicone and cross-linked OV-1701, 7% cyanopropyl, 7% phenyl methyl silicone, were tested at 143°C with 4-chlorophenol, *n*-dodecanol and acenaphthylene (Table II). The polar phenol is shifted more in the presence of the CN dipole while the polarizable acenaphthylene shows an even greater shift for 50% phenyl. The similar shifts for dodecanol show the interplay between dispersion due to the alkyl chain and the polarity of the hydroxyl. The results also show that OV-1701 is not an acceptable substitute for 50% phenyl methyl silicone.

TABLE II

RETENTION INDEX SHIFTS ON OV-1701 AND 50% PHENYL METHYL SILICONE COMPARED TO CROSS-LINKED METHYL SILICONE AT 143°C

Compound	ΔI	
	50% Phenyl	OV-1701
4-Chlorophenol	180	250
<i>n</i> -Dodecanol	110	115
Acenaphthylene	310	180

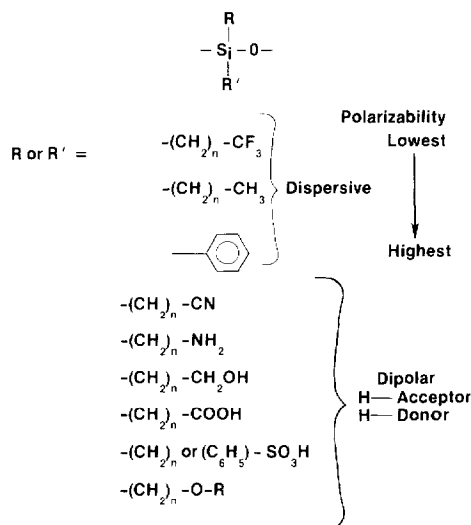


Fig. 3. Substituents for selective silicone stationary phases.

Having differentiated dispersive and polar behavior, let us now look at potential substituents for our selective phases. In Fig. 3 the substituents are divided between dispersive and dipolar; however, it should be realized that all of the substituents will have a dispersive component and the dipolar groups all have varying amounts of acid and base components. We have chosen to exclude groups that separate by shape or size, *i.e.*, liquid crystals, although their inclusion would have intriguing possibilities. The interaction indices in Table III are selected from the compilation by Burns and Hawkes⁴. The values based on calculations or estimates can be used to guide us in estimating the dispersive, δ_d , dipolar, P, base, H, and acid, Ac, components for the substituents.

Trifluoromethylalkyl heads off the list in Fig. 3 as the weakest of the dispersive substituents; however, the ability to interact specifically with electron lone pairs on carbonyl and nitro is well established, and there is also a weak dipole. Next are the alkyl phases; choosing an alkyl group longer than methyl would afford greater dis-

TABLE III

SUGGESTED DISPERSION, POLARITY, BASE AND ACID INDICES FOR GC STATIONARY PHASES (SELECTED FROM TABLE I⁴)

Stationary phase	δ_d	P	H	Ac
Dimethyl silicone	9.0	0	0	0
Phenyl methyl silicone	11.6	0	0	0
Polyethylene glycol	8.6	8	4	0
3-Cyanopropyl silicone	10.4	11*	3*	0
3,3,3-Trifluoropropyl silicone	8.6	3	0	1
1,2,3-Tris(cyanoethoxy)propane (TCEP)	8.4	11	3*	0
Trimer acid**	8.5	3	6	3
Diglycerol	8.8	9	9	4

* Estimated by analogy.

** Trimers of diterpene acid, abietic acid and related compounds isolated from pine resin [approximately $\text{C}_{54}(\text{COOH})_3$].

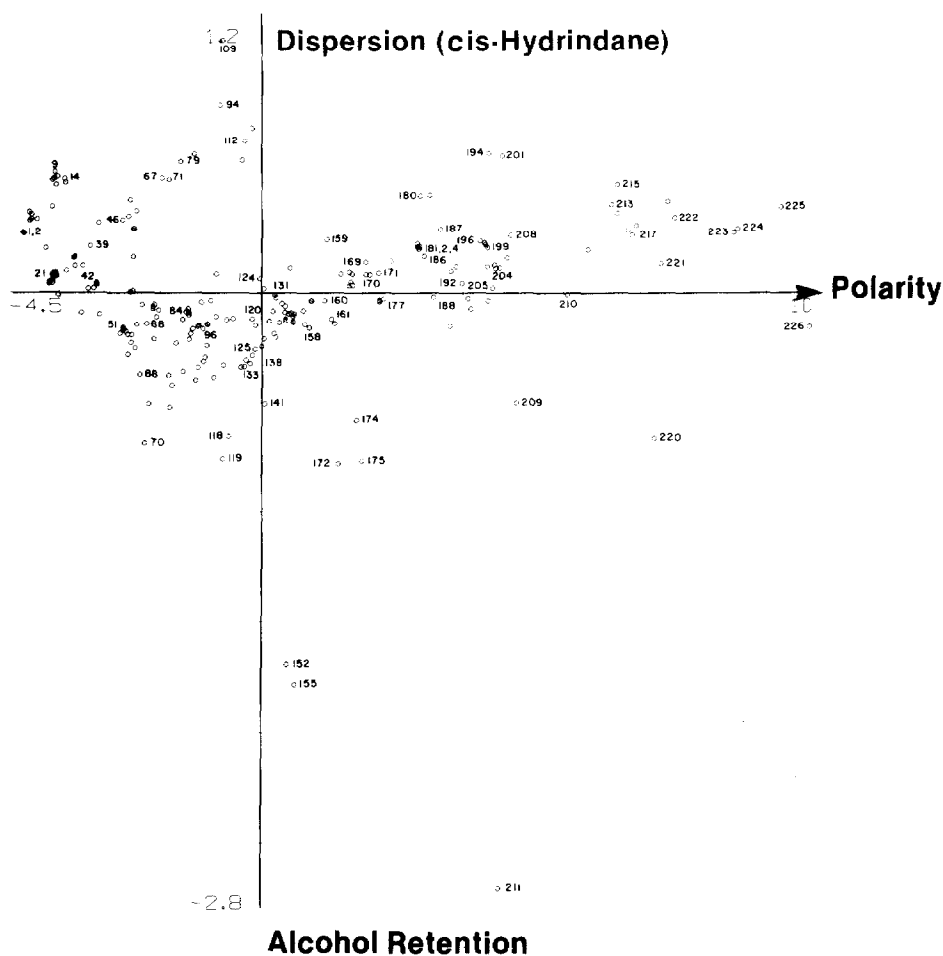


Fig. 4. Planar representation of principal component analysis of stationary phase variance. Reprinted with permission from ref. 3.

persion but would result in lower thermal oxidative stability. Phenyl or aryl phases offer stronger dispersion forces; incorporation of alkyl substituents on the ring can tailor selectivity but again thermal oxidative stability is a concern¹⁴. Hence trifluoropropyl, methyl, and phenyl remain as the dispersion selective substituents, with the latter two affording the best thermal stability of the silicose phases. The ability to be polarized by the solute is least for trifluoropropyl and greatest for phenyl.

Cyanopropyl, at the top of the polar list with the largest dipole, is already well accepted and probably affords the best thermal stability of the group. It also exhibits strong dispersion as well as a modest level of basicity. Moving down the list to amino, hydroxyl and carboxyl substituents, affords base, amphoteric and acid properties, respectively, although all three can participate as hydrogen bond donors or acceptors to varying degrees. The sulfonic acid group, possessing the strongest acidity, is also the easiest to derivatize, offering the possibility of unique and reversible selectivities. Since strong acid groups have not been available in GC, this may be one of the best

opportunities for exciting developments in stationary phases. Finally, we come to the ether functionality, which could be a reasonable approach to replacing polyethylene glycol phases. These polar groups have been bonded to silica particles for use as liquid chromatographic (LC) phases, but they are virtually unexplored in FSWCOT, with the exception of cyanopropyl.

We will now examine the uniqueness of stationary phases in light of the preceding points. The tool that will be used is the graphical representation (Fig. 4) of the principal component analysis by McCloskey and Hawkes³. Selecting 225 phases from McReynolds' compilation² to give the largest range of selectivities, the analysis fits linear equations with normalized values of the ten McReynolds δI values as the variables. The first component, the line of best fit, accounts for 97% of the variance of these phases, and the authors felt that it corresponds roughly to polarity. However, even the most polar groups have significant δ_a terms, and the equation has nearly equal coefficients for all ten ΔI values despite the range of polarities of probe molecules from nitropropane to 2-octyne and *cis*-hydrindane. Hence, we feel the first component may correspond to some combination of dispersive and polar forces.

The second component, when plotted against the first, defines the plane of best fit, accounting for 98.5% of the variance among the 225 phases. This component has positive coefficients for benzene, iodobutane, 2-octyne and *cis*-hydrindane, with the latter being substantially the largest. This suggests that dispersion is increasingly important for phases at the top of the graph, but it should be noted that a more specific phenyl-*cis*-hydrindane interaction is possible, since the phases at the very top are phenyl silicones. Because the two alcohols have large negative coefficients, alcohol retention becomes increasingly greater toward the bottom of the graph. Several of the phases toward the bottom of the graph are hydroxy phases, such as diglycerol and N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine (THEED) which have similar alcohol retention but very different dispersion.

The third component, the distance of the phases from the plane, accounts for very little of the variance. However, a few phases with unusually large distances are unique, such as the fluorinated phases due to their retention of pentanone and nitropropane coupled with poor retention of *cis*-hydrindane.

Squalane is the farthest to the left with the lowest polar component, and the methyl and phenyl silicones are all in the upper left quadrant (Fig. 5). Moving to the right we find 25% cyanoethyl XE-60 and 25% cyanopropyl 25% phenyl OV-225 at nearly the same polarity value of 1, but with XE-60 displaced toward alcohol retention and OV-225 toward dispersion/*cis*-hydrindane. XF-1150 is farther right at 3.1, and, finally, at the far right is N,N-bis(2-cyanoethyl)formamide (BCEF) with a polarity value of 9.8.

Several phases of current interest were not available at the time of McReynolds' study, but have since had McReynolds constants published for at least the first five compounds. Using these values and the indices from Table III, we can estimate the first component location of these phases. Of particular interest is the placement of the high-cyano-content silicones, SP-2340, Silar 10C and OV-275.

The points for SP-2340 and Silar 10C fall at approximately 8.5, near 1,2,3-tris(2-cyanoethoxy)propane (TCEP), while OV-275 at 10.2 is beyond even BCEF, despite the fact that all the silicones have bis-cyano substitution. There are two possible solutions of this riddle. First, the monomers used to synthesize the phases may

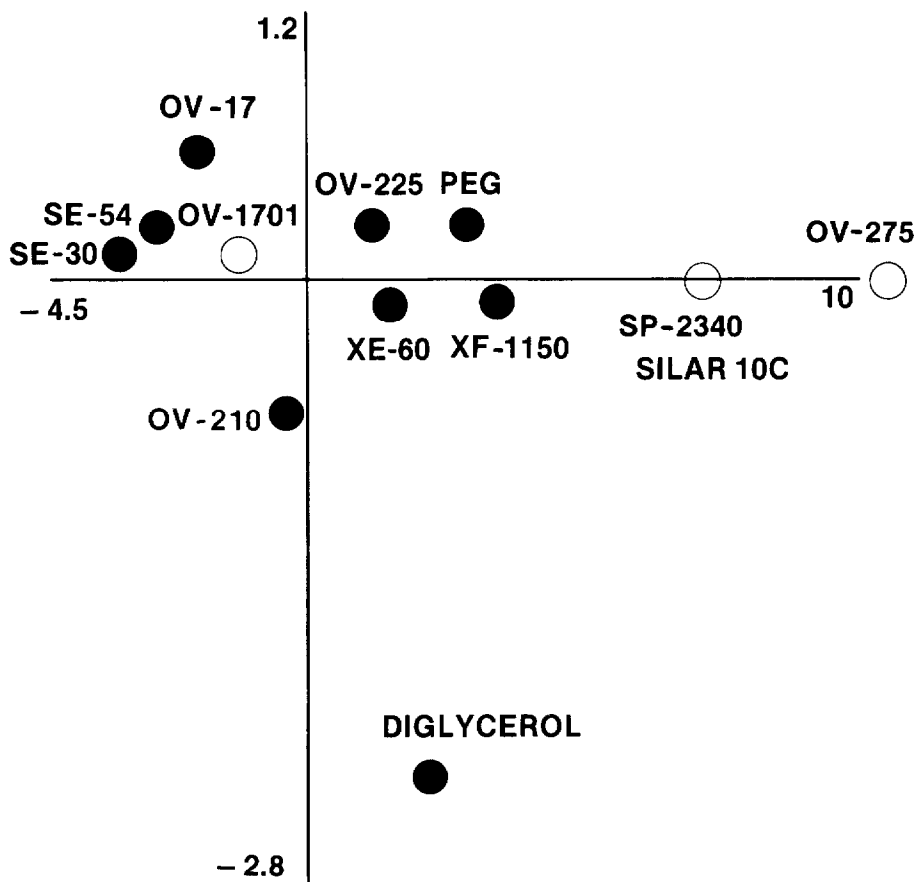


Fig. 5. Location of selected phases on the principal component plane.

solutions of this riddle. First, the monomers used to synthesize the phases may be different; some confusion exists about what monomers are used to produce OV-275. Alternatively, differences in chain length can explain the differences. All of the phases are trimethylsilyl-terminated, but OV-275 has about five times the average molecular weight of other two. The molecular weights, determined by gel permeation chromatography (GPC), to estimate chain length, suggest 80% cyano substitution for SP-2340 and Silar 10C but 95% for OV-275. Therefore, a bis-cyanopropyl gum with 75–90% cyano groups should be far out on the polarity axis.

The point for OV-1701 would be placed at about -1.6 on the polarity axis, corresponding to about 40% phenyl. However, as the results discussed above have demonstrated, it would be placed much lower on the dispersion/alcohol axis due equally to lower dispersion and increased alcohol retention. This is much lower on either of the axes than the polyethylene glycols (PEGs), which, as one author recently suggested, might be replaced by OV-1701¹⁵. In fact, the placement of PEG above XF-1150 and to the right of OV-225 suggests that a silicone of 40–45% cyanopropyl and 20–25% phenyl substitution may give selectivity close to that of Carbowax.

For the final point of this report, returning to the phenyl silicones will provide

an example of the need for the characterization of polymeric phases. Measurements have been made of the UV absorption of OV-17, the new OV-17 gum and an experimental 50% phenyl gum of high molecular weight. Using the gums, which contain 49–50% phenyl substitution, as reference, the calculated molar absorbance at 264 nm is consistent with 41–42% phenyl substitution for OV-17. Similar to the case of the cyano phases, OV-17 is trimethylsilyl-terminated and, using the published molecular weight, we can calculate the phenyl substitution at 41–42%. Returning to Fig. 2, OV-17 is the point plotted as 50%, which falls to the right of the curve; however, plotted as 42%, the point would fall on the curve. The UV absorption measurements also indicate that several of the commercially available phenyl methyl silicones may have phenyl contents different from those commonly accepted. In some cases this can be accounted for by simple chain length calculations as above, whereas for others different methods of specifying the composition may have been used. The percentages used in this report are based on the total number of substituent groups in the phase.

We are firmly convinced that it is critical for selective silicone stationary phases to exhibit defined behavior consistently. The phases must be thoroughly characterized by chromatographic behavior and relevant analytical techniques. In our laboratory, we routinely compare UV absorption measurements, GPC and thermal analysis for each bottle of phase received. Additionally, a sampling plan is utilized to compare eight FSWCOT columns randomly with eight columns made from one bottle of a phase of known performance. In the future we hope to include infrared and nuclear magnetic resonance spectroscopy in the characterization. It may also be fruitful to measure diffusivities for any new gums, owing to the wide range of diffusivities as different substituents are added. It is imperative that the molecular weight and the chemical composition be specified to insure true composition and reproducibility of crosslinking.

CONCLUSIONS

Having embarked upon optimizing stationary phases for the inert, smooth, fused-silica capillary columns available today, we have reviewed some of the concepts advanced to delineate uniqueness for selection of preferred stationary phases. Until recently, monomeric phases were frequently included, but they are quite impractical for our needs. With the advent of improved silicones, substitutes became available but many of them were fluids designed for coating GC packings. As discussed, there are still major problems in determining their composition and achieving reproducible properties in capillary columns.

A subtle set of interactions determines relative and absolute retention behavior of elutes in GC columns. However, the use of the simple, planar, principal component representation of stationary phase variance allows the estimation of compositions giving the greatest range of selectivity. It can, thereby, be concluded that the order of optimized phases, all high-molecular-weight cross-linkable gums, would be: (1) methyl silicone, (2) 50–70% phenyl methyl silicone, (3) cyanopropyl methyl silicones of medium (25–50%) and high (70–90%) cyanopropyl incorporation, (4) trifluoropropyl methyl silicone, and (5) PEG or a silicone, as suggested above. There does not seem to be a clear preference for the incorporation of phenyl in the medium cyanopropyl; therefore, the possible trade-off of dispersion selectivity *vs.* thermal

stability will have to be considered, as well as the question of a possible substitute for PEG. The lack of an acid component in the list of optimized phases should not be overlooked; incorporation of the sulfonic acid functionality may have something to offer in this respect. Finally, there are the rest of the dipolar substituents awaiting further development.

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