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SYSTEMATIC APPROACH TO STATIONARY PHASE SELECTION IN GAS CHROMATOGRAPHY

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SUMMARY

A method is presented for selecting gas chromatographic (GC) stationary phases, based on both selectivity and strength parameters. This scheme indicates that additional liquid phases are needed not only for improved stability, but, more importantly, for selectivity in two of the three corners of the selectivity triangle. The method can be automated for computer-controlled GC optimization.

INTRODUCTION

In gas chromatography (GC), resolution, R_s, is usually optimized by increasing the number of plates, N

$$R_s = \left(\frac{\sqrt{N}}{4} \right) \left(\frac{\alpha - 1}{\alpha} \right) \left(\frac{k'}{1 + k'} \right) \qquad (1)$$

(α = separation factor, k'_2 = capacity factor) often through use of capillary columns. Greater benefits can be realized by changing α for poorly resolved peaks than by increasing N. When α increases from 1.05 to 1.10, while all other variables are constant, R_s almost doubles. This corresponds to an approximately four-fold increase in N and analysis time, if the column length is changed to achieve the same increase in R_s. As α approaches 1, no practical increase in N will increase R_s enough to resolve the components: changing α is the only choice. When α is increased, separation of highly complex mixtures, faster analyses and increased sample capacity can be expected.

In GC, α can be changed dramatically by using stationary phases with unique selectivities. Two stationary-phase attributes that have been used for selecting GC columns are selectivity and strength. However, these terms are often interchanged

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and confused with the term "polarity". The object of this paper is to present a clear, systematic method for GC liquid-phase selection, based on a classification of phases based on both strength and selectivity.

Rohrschneider[1] classified liquid phases on the basis of their ability to retard probe solutes. This system was further developed by McReynolds[2]. The Rohrschneider/McReynolds (R/M) system compares the retention indices on a particular phase with the indices on squalane, a hydrocarbon phase. The information is tabular, and the differences between phases are not apparent, since the indices, in general, change monotonically with increasing "polarity". However, one cannot make *a priori* predictions of absolute retention, since indices are relative values.

Another approach to GC phase selection was given by Semenchenko and Vigdergauz[3], who classified stationary phases into seven different types, based on five different polarity factors. Their calculations were based on R/M indices. This approach permits one to predict selectivity differences of liquid phases.

Novak *et al.*[4] and Risby and co-workers[5,6] characterized liquid phases by thermodynamic parameters. These approaches have been quite useful and, for monofunctional phases, have the potential of predicting specific retention volumes of a particular solute in the tested liquid phase. Other classification schemes have been proposed by Fellous *et al.*[7] (factor analysis), De Beer and Heyndrickx[8] (numerical taxonomy), Ševčík and Löwentap[9] (ratio of retention time differences), Laffort and Patte[10] (solubility factors) and Karger *et al.*[11] (expanded solubility parameters).

A more useful approach was developed by Snyder[12], who proposed the characterization of chromatographic phases by the relative strength of hydrogen-bonding interactions (proton donor and proton acceptor) and dipole interactions. A measure of these interactions, selectivity parameters, is obtained from R/M indices for three test solutes, ethanol, 1,4-dioxane and nitromethane.

EXPERIMENTAL

Instrumentation

Hewlett-Packard (Avondale, PA, U.S.A.) Model 5710 and 5880 chromatographs with thermal conductivity detectors were used for retention index measurements at 120°C. Data were obtained from the 5880 microprocessor or, in the case of Model 5710, from the PDP-10 computer (Digital Equipment, Maynard, MA, U.S.A.) of our Central Research and Development Department[13].

Column packings

Packings were prepared by dissolving a liquid phase (10%, w/w) in an appropriate solvent. The support (Supelcoport, 100–120 mesh; Supelco, Bellefonte, PA, U.S.A.) was added, and the solvent was removed by evaporation under nitrogen with gentle stirring. If necessary, the packings were further dried in a vacuum oven. The coated supports were packed into 1.8 m × 3 mm stainless-steel tubes by the tapping method. The columns were conditioned by slowly increasing the column temperature to 150°C and holding it there overnight. The helium carrier gas was set at 30 ml/min.

Sampling

The test solutes (ethanol, dioxane and nitromethane) were kept in septum vials.

Approximately 20 μl of headspace vapor were removed with a gas-sampling syringe and injected onto the column for each solute. Averages of at least five measurements per probe were determined on each phase. The headspace air peak was used for dead time (t_0) measurements.

Selectivity calculations

Kováts indices[14] were calculated from adjusted retention times for each probe solute on each stationary phase. Corrected indices for the solutes on a deactivated squalane column were substracted to determine the ΔI values. Selectivities, x_i, were calculated and plotted on the face of the selectivity triangle[12] by using the equation:

$$x_i = \frac{\Delta I_i}{\Delta I_e + \Delta I_n + \Delta I_d} \tag{2}$$

Where ΔI_i, ΔI_e, ΔI_n and ΔI_d are the differences in retention indices for probe solute, ethanol, nitromethane and dioxane, respectively. The denominator of this ratio reflects excess retention due to polar interactions; the larger the $\Sigma \Delta I_i$, the more significant the polar contribution of the stationary phase to retention of a solute.

Calculation of the corrected retention indices on squalane

The corrected retention indices for the three probe solutes on squalane were estimated from a series of experiments on column wall, support and *in situ* deactivation[15]. These corrected values ($I_e = 280$, $I_n = 415$, $I_d = 645$) were used in all calculations and represent the dispersive component of the probe solutes. Changes in these values will be significant only for liquid phase with small $\Sigma \Delta I$.

RESULTS AND DISCUSSION

In classifying stationary phases, it is necessary to select solute molecules that will test the most significant retention mechanisms. We selected the probe solutes used in Snyder's solvent classification scheme[16] (data originally from Rohrschneider[17]). The probes ethanol, 1,4-dioxane and nitromethane are volatile and represent the three common retention mechanisms: hydrogen-bond donor, hydrogen-bond acceptor and dipole interactions, respectively. The selectivity parameters and the $\Sigma \Delta I$ values for eight liquid phases are given in Table I. Fig. 1 shows the location of three different methyl and methyl/phenyl silicones and 1-hexadecanol on the selectivity triangle. The circles outline areas where molecules with similar polar functional groups are clustered[12]. Methyl silicone falls in group II (ethers) and 1-hexadecanol falls near group I (alcohols). As phenyl groups are substituted for methyl groups (SE-52, 5% phenyl; OV-17, 50% phenyl), the selectivity of the pases moves towards group VII (aromatics), indicating that selectivity may be tailored by mixing some functional groups.

Table I shows that the $\Sigma \Delta I$ values also increase as the phenyl/methyl ratio increases, indicating that the proportion of polar *versus* non-polar interactions increases with polar functional group density.

Changes in selectivity and $\Sigma \Delta I$ can be used to monitor degradation of stationary phases. In the case of stationary phases with a single kind of polar functional
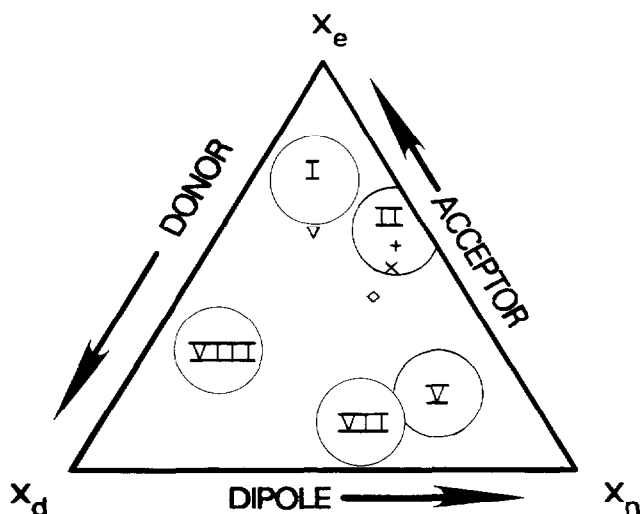
Fig. 1. Expanded selectivity triangle, showing several liquid phases and functional group locations, as a function of selectivity parameter, x_i. Dipole and acceptor axes from 0.2 to 0.7, donor axis from 0.1 to 0.6. Alcohols, group I; ethers, group II; chlorinated hydrocarbons, group V; aromatics, group VII; weak acids, group VIII. Group locations from ref. 12. Liquid phases: +, SE-30; ×, SE-52; ◇, OV-17; ▽, hexadecanol.

group, as some of those functional groups are lost (cleaved), $\Sigma\Delta I$ decreases, but selectivity does not change. If, on the other hand, functional groups are changed, *e.g.*, oxidized, or if one type of group is preferentially lost, in the case where there are mixed functional groups, both the selectivity and the $\Sigma\Delta I$ will change.

A test mixture was chromatographed on squalane and the three different silicone stationary phases to study selectivity effects. The test mixture contained a proton donor (2-propanol), a proton acceptor (triethylamine), a weak dipole (1,2-dichloroethane), a strong dipole (acetonitrile) and octane, which has no polar interactions. Table II lists physical properties of these test solutes. As can be seen in Fig. 2, the elution order on squalane is due to dispersive forces (boiling point, molar volume). Even though methyl silicone selectively favors proton donors (it is in the proton-acceptor region of the selectivity triangle), the major contribution to retention is due to dispersive interactions (low $\Sigma\Delta I$), and the elution order is the same as on squalane. As the ratio of phenyl to methyl groups increases, the silicone phases become less selective proton acceptors. With OV-17, polar contributions to retention become significant ($\Sigma\Delta I = 952$), and the interaction with dipoles and proton donors is exhibited primarily by increased retention of the dipoles (peaks 1 and 3) relative to triethylamine and octane (peaks 4 and 5).

TABLE I

GC STATIONARY PHASE SELECTIVITIES

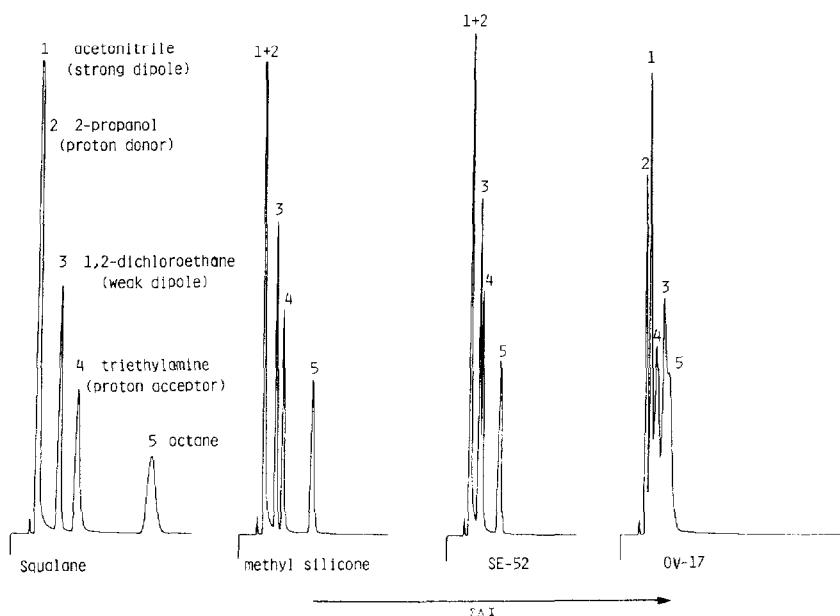| Phase	I	x_e	x_n	x_d
Methyl silicone	310	0.477	0.384	0.139
SE-52	475	0.451	0.392	0.158
OV-17	977	0.415	0.392	0.193
QF-1	1064	0.304	0.455	0.242
Carbowax 20M	1759	0.348	0.412	0.239
Polyethyleneimine	1988	0.438	0.347	0.216
Silar 10 CP	2421	0.326	0.406	0.268
1-Hexadecanol	629	0.493	0.293	0.215

Fig. 2. Chromatograms of the test mixture on several stationary phases. Total analysis time decreases with increase in "polarity" under the same experimental conditions.

Of particular note is the fact that, as the polarity of the stationary phase increases (larger $\Sigma \Delta I$), the total time for the separation of this test mixture *decreases*. Only the relative retention of the polar molecules is larger with respect to the normal alkanes, *e.g.*, octane. This illustrates how the McReynolds numbers ($\alpha \Sigma \Delta I$ used here), commonly used as a measure of "polarity", can be misleading.

The selectivities of four liquid phases, including SE-30, are plotted in Fig. 3. Most commercial phases fall into the enclosed portion at the bottom center of the selectivity triangle, but outlying phases include polyethyleneimine (PEI) and QF-1. The same five liquid phases are plotted in Fig. 4, where $\Sigma \Delta I$ has been added as the third dimension. As $\Sigma \Delta I$ increases, polar interactions become more significant in the retention of a polar solute. The largest change in α for poorly resolved polar solutes can be achieved by using stationary phases the selectivities of which lie in corners of the triangle and have large $\Sigma \Delta I$ values.

Carbowax 20M and Silar 10 CP have a similar selectivity toward proton donors and dipoles. As can be seen from the chromatogram in Fig. 5, the dipole probes interact more strongly with Silar 10 CP than with Carbowax 20M: the strong dipole, acetonitrile, is retained longer than the higher-boiling, weak dipole, dichloroethane.

TABLE II

PHYSICAL PROPERTIES OF TEST MIXTURE SOLUTES

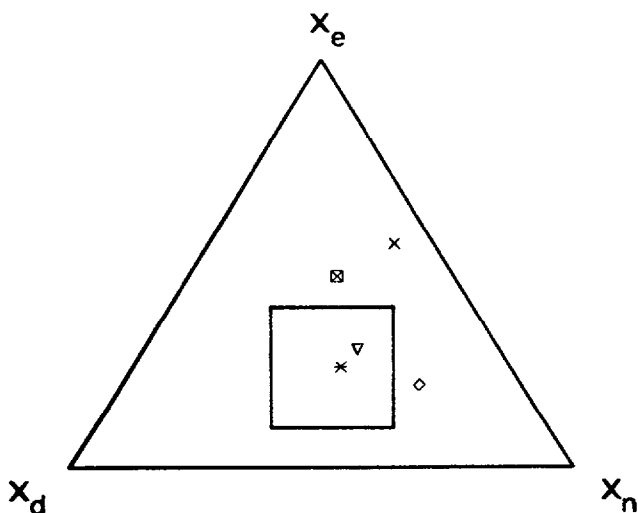| Solute	Boiling point (°C)	Molar volume (ml/mole at 20°C)	Dipole moment (Debye)
Acetonitrile	81.6	52.5	3.44
2-Propanol	82.3	76.5	1.66
1,2-Dichloroethane	83.5	79.0	1.86
Triethylamine	89.3	139.1	0.66
Octane	125.7	162.6	0.0

Fig. 3. Selectivity triangle, showing location of five stationary phases. The most common "polar" phases, Carbowax 20M (▽) and Silar 10 CP (∗), are not very selective. Other phases: ×, SE-30; ◇, QF-1; ⊠, PEI.

Two commercial phases with selectivities significantly different from most GC phases, PEI and QF-1, fall outside the enclosed region on Fig. 4 and have relatively large $\Sigma \Delta I$ values. The benefits of the selective interactions of these two phases can be seen in Fig. 6. For QF-1, acetonitrile is the most highly retained, and the proton donor and acceptor (2-propanol, peak 2, and triethylamine, peak 4) are least strongly retained.

Even though the $\Sigma \Delta I$ for QF-1 is much lower than that for Silar 10 CP, the fact that the selectivity parameters place it closer to the dipole corner of the triangle means that it interacts more selectively with dipoles than with the other probe molecules. This effect demonstrates the power of using liquid phases with unique selectivities.

For PEI, a strong proton acceptor, the proton donor 2-propanol (peak 2) is most strongly retained, whereas triethylamine and acetonitrile are more weakly retained. The fact that the $\Sigma \Delta I$ for PEI is so high is evidenced by the early elution of
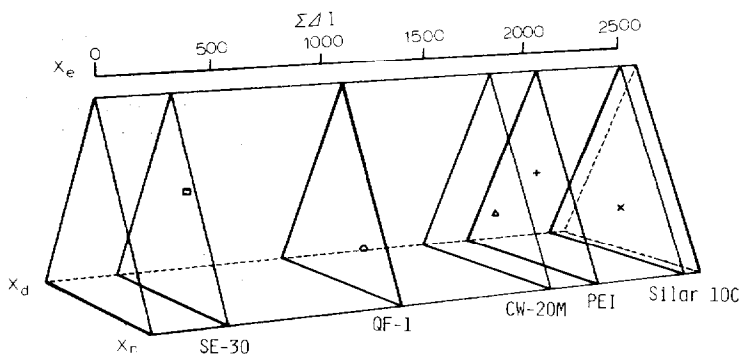

Fig. 4. Same phases as in Fig. 3 plotted vs. $\Sigma \Delta I$. Phases with higher $\Sigma \Delta I$ have a higher proportion of polar vs. non-polar interactions and tend to exhibit any inherent selectivity. CW-20M = Carbowax 20M.
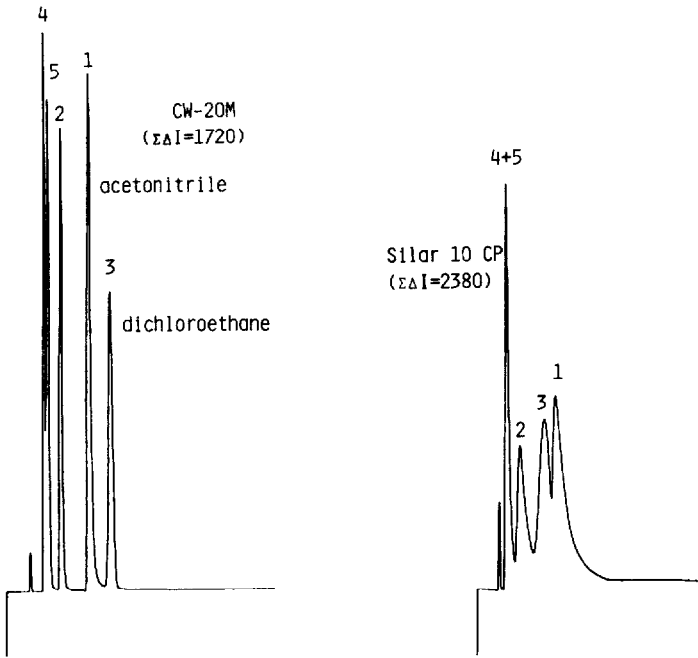
Fig. 5. Chromatograms of the test mixture on Carbowax 20M and Silar 10 CP. Even though their selectivities are similar, Silar 10 CP exhibits its selectivity toward dipoles and proton donors more than Carbowax 20M due to a larger $\Sigma \Delta I$. Peak numbers as in Fig. 2.
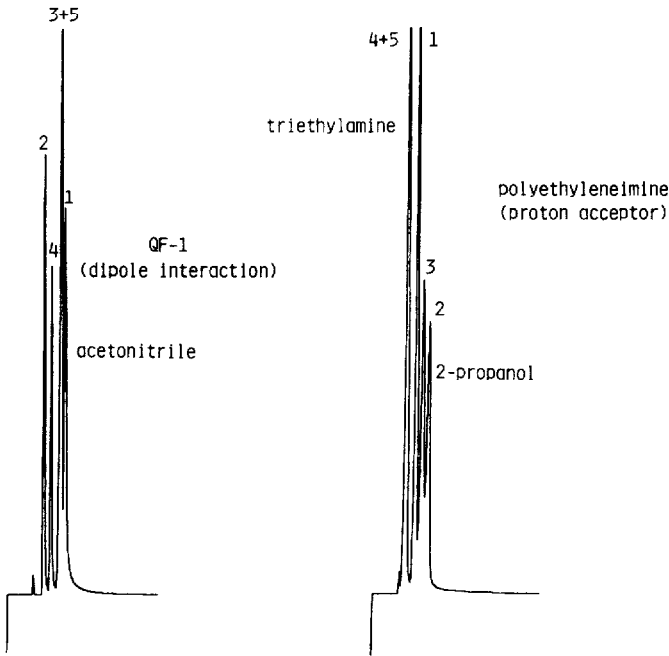

Fig. 6. Chromatograms of the test mixture on QF-1 and polyethyleneimine. QF-1 is selective toward dipoles, whereas polyethyleneimine is selective toward proton donors. Peak numbers as in Fig. 2.

octane (peak 5) ($\Sigma\Delta I$ values are indexed to the retention of n-alkanes) with respect to the polar solutes, yet the full analysis time is still less than it is for the same test mixture, chromatographed on squalane, as is seen for the silicone phases.

For optimized selection of GC liquid phases, representative phases (or combinations of phases) with large $\Sigma\Delta I$ values and lying in the corners of the selectivity triangle are needed. Such a selection would allow procedures similar to those that have been used for optimizing LC mobile phases[18] to be used for the selection of the best GC stationary phase for separating a given sample.

The phases with unique selectivities toward dipoles include the trifluoropropyl silicones (QF-1, OV-210, SP-2401) which have terminal fluorine atoms on the propyl groups. In the proton-acceptor corner of the triangle there are few good candidates. We have found PEI and polypropyleneimine the most promising, although they are unstable. There are no good commercial phases in the proton-donor corner of the triangle. For midpoint phases, one can use the readily available Carbowax 20M and OV-17 phases, or a mixture of phases from the apices of the selectivity triangle.

Once an optimum phase is determined by using standard methods, the total analysis time is optimized by adjusting the phase loading, column length or most conveniently the temperature. Although computerized optimization has not been attempted, hardware and software developed for optimizing mobile and stationary phases in liquid chromatography[18,19] could undoubtedly be used.

Both commercially available and newly synthesized polymers are being evaluated with respect to their selectivities and performance in the hope that they lie in corners of the selectivity triangle and fulfill the requirements of good GC stationary phases. Once suitable phases have been found, effects of mixing stationary phases, and the utility of computerized optimization will be assessed.

ACKNOWLEDGEMENTS

REFERENCES

1 L. Rohrschneider, *Advan. Chromatogr.*, 4 (1967) 333.
2 W. O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
3 L. V. Semenchenko and M. S. Vigdergauz, *J. Chromatogr.*, 245 (1982) 177.
4 J. Novak, J. Ruzickova, S. Wicar and J. Janak, *Anal. Chem.*, 45 (1973) 1365.
5 T. H. Risby, P. C. Jurs and B. L. Reinbold, *J. Chromatogr.*, 99 (1974) 173.
6 B. L. Reinbold and T. H. Risby, *J. Chromatogr. Sci.*, 13 (1975) 372.
7 R. Fellous, D. Lafaye de Michaux, L. Lizzani-Cuvelier and R. Luft, *J. Chromatogr.*, 248 (1982) 35.
8 J. O. de Beer and A. M. Heyndrickx, *J. Chromatogr.*, 235 (1982) 337.
9 J. Ševčik and M. S. H. Löwentap, *J. Chromatogr.*, 217 (1981) 139.
10 P. Laffort and F. Patte, *J. Chromatogr.*, 126 (1976) 625.
11 B. L. Karger, L. R. Snyder and C. Eon, *Anal. Chem.*, 50 (1978) 2126.
12 L. R. Snyder, *J. Chromatogr.*, 92 (1974) 223.
13 J. S. Fok and E. A. Abrahamson, *Amer. Lab.*, 7 (1975) 63.
14 A. Wehrli and E. Kováts, *Helv. Chim. Acta*, 42 (1959) 2709.
15 M. S. Klee, M. A. Kaiser and C. K. Nguyen, in preparation.
16 L. R. Snyder, *J. Chromatogr. Sci.*, 16 (1978) 223.
17 L. Rohrschneider, *Anal. Chem.*, 45 (1973) 1241.
18 J. L. Glajch, J. J. Kirkland, K. M. Squire and J. M. Minor, *J. Chromatogr.*, 199 (1980) 57.
19 J. L. Glajch, J. J. Kirkland, J. C. Gluckman, J. G. Charikofsky and J. M. Minor, in preparation.