Journal of Chromatography, 504 (1990) 186–190
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 22 246

Note

Implications of solvent selectivity triangles in assessing stationary phases for gas chromatography

T. J. BETTS
School of Pharmacy, Curtin University of Technology, GPO Box U1987, Perth, W.A. 6001 (Australia)
(First received December 15th, 1989; revised manuscript received January 3rd, 1990)

Poole and Poole[1] have recently reviewed the characterization of solvent properties of gas chromatography (GC) liquid stationary phases. Referring to the use of Snyder's solvent selectivity triangle[2] which they note "has strong visual impact" they comment that this "original choice of (solvents for triangular) axes for proton-donor-acceptor and orientation interactions ... is quite reasonable". Snyder's probe solutes used for studies of GC stationary phases were ethanol, nitromethane (Y and U respectively as designated by Rohrschneider[3]) and dioxane (l′ by McReynolds[4]) and Kersten and Poole[5] in 1988 found that "the retention of ethanol and nitromethane on the non-polar GC phases is inadequate" even at their low temperature of 80.8°C. They also found that "dioxane is a rather insensitive probe for proton-donor interactions ... New probes should be selected". Poole thus ignores his own observations in the review[1] allowing him to reuse his previous triangular figures. The earlier paper[5] comments that "*n*-butanol, nitropropane, 2-pentanone and pyridine (McReynolds' y′, u′, z′ and s′, respectively) ... are better retained on most phases. These additional probes can be used to determine whether the choice of the test solute influences the position of a particular phase in the solvent selectivity triangle". As only three probes must be used to construct such a triangle, it seems self-evident that their choice must do so and I have examined this here. Kersten and Poole[5] noted that (Snyder's) nitromethane does not behave characteristically of the other nitroalkanes on most selective (GC) phases. "The use of higher molecular weight nitroalkanes in place of nitromethane will significantly change the relative position of a phase in the selectivity triangle". They further comment "that both pyridine and 2-pentanone have reasonably large dipole moments compared to dioxane and consequently their retention will be more influenced by orientation interactions"[5]. It seems desirable to use these two solutes in solvent triangles.

Poole and Poole note my work[6] using *n*-butanol, pyridine and 2-octyne (McReynolds' k′) for a selectivity triangle with the comment "it is not clear what advantage was gained by the change. 2-Octyne measures mainly dispersive interactions so that ... the triangle is changed"[1]. It was chosen because, of the McReynolds solute probes, it gave the best spread of results in the triangle —surely a good reason? This allowed me to perceive three groups of stationary phases: (1) fully methyl polysiloxanes such as OV-1, SE-30, SP-2100; and phenyl–methyl (nominally 50:50)

0021-9673/90/$03.50 © 1990 Elsevier Science Publishers B.V.

polysiloxanes like OV-17 or SP-2250, with the sequence of probes being butanol–pyridine–*octyne*. (2) More polar polysiloxanes such as cyanopropyl–phenyl–methyl (25:25:50) like OV-225; and the trifluoropropyl–methyl (50:50) ones like OV-210, with the sequence of probes being butanol–octyne–*pyridine*. (3) Highly polar phases such as cyanopropyl–methyl (90:10) polysiloxanes like SP-2330; polyethylene glycols (PEG) (20M and 1500) and diethylene glycol succinate, with the sequence of probes being octyne–*butanol*–pyridine.

If such results can indicate that only three phases may be enough for most purposes —possibly three different polysiloxanes— surely this justifies the choice of solute probes?

Kersten and Poole[5] detected but did not enclose four selectivity groups in their Snyder triangle (using the undesirable ethanol, nitromethane and dioxane), given below in my sequence and labelling: (A) phenyl–methyl (50:50) such as OV-17; and trifluoropropyl–methyl (50:50) polysiloxanes (QF-1). (B) Cyanopropyl–methyl (25:75?) polysiloxanes like the unusual OV-105. (C) Cyanopropyl–phenyl–methyl (25:25:50) polysiloxanes like OV-225; and polyethylene glycols (20 M). (D) Thiocyanates —synthesised by them; not widely used.

Apart from the thiocyanates, the other groups all show the same probe sequence of ethanol–nitromethane–dioxane, suggesting these solutes are a poor combination.

Although for some reason they did not study fully methyl polysiloxanes, nor Apiezons, nor diethylene glycol succinate they still failed to note what I previously pointed out[6], that the most polar (thiocyanate) phases were nearest to the centre of the selectivity triangle, and the lower polarity groups A and B furthest from the centre. "A phase exhibiting minimum selectivity would be located at the centre of the triangle. The most selective phases are found towards the corners of the triangle"[5]. This can be achieved by applying bias to the triangle axes —Kersten and Poole use 0.2–0.7 for ethanol and nitromethane, but 0.1–0.6 for dioxane, these being not quite the same axis values as those of Snyder[2].

PROCEDURE

To check this possibility that strongly polar phases might be indicated triangularly to be less selective than those of low polarity, I plotted selectivity triangles using published McReynolds values[4] for different combinations of three of his first five solutes. The combination of benzene–butanol–nitropropane gave poor discrimination as every GC phase yielded the probes in this sequence. Other combinations gave different degrees of discrimination and butanol–nitropropane–pyridine was selected. It is interesting that two of these solutes were probes I selected previously in 1986[6].

Values for each of these probes were calculated by

$$x = (\overline{\mathrm{McR}}_{\mathrm{solute}})/\Sigma(\overline{\mathrm{McR}}_{\mathrm{three\ solutes}})$$

where $\overline{\mathrm{McR}}$ are the McReynolds values published[4] and these are given in Table I and plotted in a biased triangle in Fig. 1.

DISCUSSION

It is clear in Fig. 1 that strongly polar phases are clustered together near to the centre of the selectivity triangle, which can be included with them in a circle of radius

TABLE I

PROPORTIONS (x) OF THE SUM OF THREE RECORDED McREYNOLDS VALUES, OR FROM KERSTEN AND POOLE[5]

$\overline{McR}$ = McReynolds value published[4]; PSX = polysiloxane; PEG = polyethyleneglycol. x Values in italics are in the range 0.327–0.335 (around the "mid" value of 0.333). $\overline{K/P}$ = Values calculated according to McReynolds procedure from data[5]; bu = butanol; di = dioxane; et = ethanol; nim = nitromethane; nip = nitropropane; py = pyridine.

No.	*Stationary phase*	*n-Butanol*		*Nitropropane*		*Pyridine*		$\Sigma\overline{McR}$	*Probe solute sequence*
		$\overline{McR}$	x	$\overline{McR}$	x	$\overline{McR}$	x		
1	Apiezon L grease	22	0.229	32	*0.333*	42	0.438	96	bu-nip-PY
2	PSX-fully methyl (SE-30, OV-1, SP-2100)	53	*0.335*	64	0.405	41	0.260	158	py-BU-nip
3	PSX-phenyl–methyl (50:50) (OV-17, SP-2250)[a]	158	0.262	243	0.403	202	*0.335*	603	bu-py-NIP
4	PSX-phenyl–methyl (75:25) (OV-25)	204	0.258	305	0.387	280	0.355	789	bu-py-NIP
5	PSX-trifluoropropyl–methyl (50:50) (OV-210, QF-1)	233	0.233	463	0.463	305	0.305	1001	bu-py-NIP
6	PSX-cyanopropyl–phenyl–methyl (25:25:50) (OV-225)	369	0.296	492	0.394	386	0.309	1247	bu-py-NIP
7	PEG 20M	536	*0.331*	572	0.353	510	0.315	1618	py-BU-nip
8	PSX-cyanopropyl–phenyl (50:50) (SP-2300)	495	0.299	637	0.383	531	0.319	1663	bu-py-NIP
9	Free fatty acid phase	580	0.321	602	*0.333*	627	0.347	1809	bu-nip-PY
10	PEG 1500	607	*0.333*	626	0.344	589	0.323	1822	py-BU-nip
11	Diethylene glycol succinate	751	0.306	840	0.343	860	0.351	2451	bu-nip-PY
12	Tris-(cyano-ethoxy)propane	857	0.306	1028	0.367	915	*0.327*	2800	bu-py-NIP
13	Bis-(cyano-ethyl)formamide	991	0.320	1110	0.358	1000	0.322	3101	bu-py-NIP
		Ethanol		*Nitromethane*		*Dioxane*		$\Sigma\overline{K/P}$	
		$\overline{K/P}$	x	$\overline{K/P}$	x	$\overline{K/P}$	x		
3′	PSX-phenyl–methyl (50:50)	139	0.238	263	0.450	182	0.312	584	et-di-NIM
5′	PSX-trifluoropropyl–methyl (50:50)	263	0.230	427	0.484	253	0.286	883	et-di-NIM
6′	PSX-cyanopropyl–phenyl–methyl (25:25:50)	383	0.311	517	0.419	333	0.270	1233	di-ET-nim
7′	PEG 20M	581	*0.330*	727	0.413	450	0.256	1758	di-ET-nim

[a] Approximate side chain percentage is indicated.

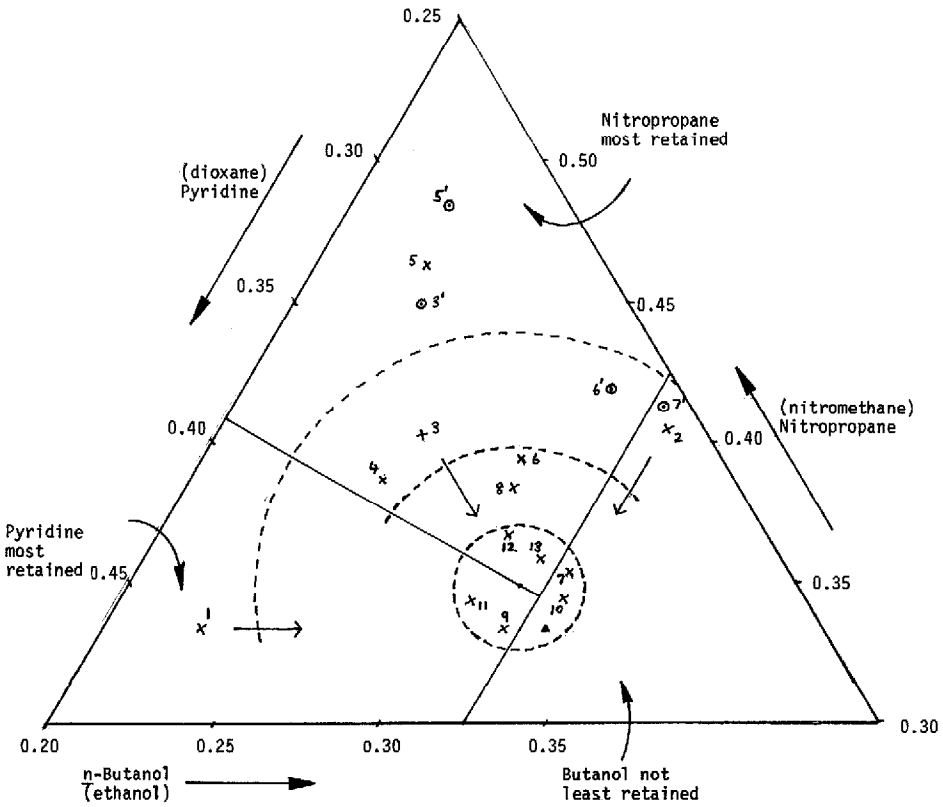

Fig. 1. Plot of McReynolds values on various gas chromatographic stationary phases (×) for the three solute probes *n*-butanol (from left side to lower right apex), nitropropane (top apex) and pyridine (lower left apex). Also shown are values from Kersten and Poole[5] for corrected I_R (retention index based on *n*-alkanes) on some of the phases (⊙) for the solutes ethanol (lower right apex), nitromethane (top apex) and dioxane (lower left apex). Numbers 1–13 refer to the phases listed in Table I. ▲ is the centre of the full triangle plot (0.333 for all three solutes).

about 0.02 drawn at about 0.318 butanol–0.333 pyridine. Phases of fairly high polarity (SP-2300 and OV-225) are outside this circle whilst lower polarity SE-30, OV-17 and OV-25 are more remote. The most distant phases are Apiezon L and OV-210, and these are directed towards the pyridine-retaining and nitropropane-retaining corners of the triangle, respectively. It is possible to draw a line at butanol 0.325 to include the phases SE-30 and polyethylene glycols for which butanol is not the least retained (probe sequence pyridine–*butanol*–nitropropane). Another line separates from the remaining phases three which retain pyridine most strongly (diethylene glycol succinate, free fatty acid phase and Apiezon L) with probe sequence butanol–nitropropane–*pyridine*. This leaves a large group with strong affinity for nitropropane and least retention of butanol (probe sequence butanol–pyridine–*nitropropane*). These solute sequence-defined groups are very like my 1986 ones[6], with nitropropane in place of octyne.

These divisions are quite odd, as each includes both low and high polarity phases. For example, fully methyl polysiloxane is grouped with the polyethylene

glycols, and Apiezon L is grouped with a polyester. What are the implications? It cannot be suggested sensibly that highly polar phases such as free fatty acid phase and PEG 1500 should be discarded as lacking solute discrimination because they plot near the 0.333 centre of the triangle. Nor is it reasonable to suggest that only phases near the apices of the triangle (Apiezon L and OV-210) should be used for their high discrimination. Perhaps phases should be selected for particular separations if they are virtually "neutral" to one of the solute probes (with a value close to 0.333) and hence preferentially retain one of the other two, so discriminating well, substances of this type retained? For example, Apiezon L (1 in Fig. 1) is neutral to nitroalkanes and selective for aromatics like pyridine, which it retains relatively strongly. It should not be chosen to resolve aliphatic alcohols. Free fatty acid phase (9) shows this to much lesser extent. Fully methyl polysiloxanes (2) are neutral to these alcohols, selective for nitroalkanes, and should not be chosen for aromatics; and this applies to PEG 1500 (10) to a lower degree. The commonly used phenyl–methyl (50:50) polysiloxanes (3) are surprisingly neutral to aromatics, selective for nitroalkanes, but not the phase of choice for aliphatic alcohols. Without exhibiting any fully "neutral" character tris-(cyano-ethoxy)propane (12) shows a reduced response of this type. Of course, this reduced discrimination response is due partly to the larger figures of McReynolds values given by the polar phases. Differences between the smaller values of the non-polar phases produce a relatively more severe displacement from the centre of the triangle.

Perhaps the best use for this plot is to indicate, for example, that Apiezon L is a low polarity alternative to diethylene glycol succinate. Similarly tris-(cyano-ethoxy)propane, OV-225, OV-17, OV-210 represent a decreasing polarity sequence of similar discriminatory potential. Corresponding results are obtained (with a somewhat different plot) using pentanone values with butanol and pyridine. Even using Kersten and Poole's results[5] for ethanol–nitromethane–dioxane and plotting them on my butanol–nitropropane–pyridine triangle gives points for the phases which remain in the same groupings (Fig. 1).

The British Pharmacopoeia 1988 (Vol. I)[7] includes over 60 examples of the use of GC on liquid phases and hence should provide a useful review of the selection of stationary phases for drug analysis. From my pyridine-retaining group, Apiezon L is only recommended twice, free fatty acid phase three times and polyester phases eight times. These phases thus form only about 22% of the GC uses. From my butanol-not-least-retained group, polyethylene glycols are recommended for twelve uses and fully methyl polysiloxanes for thirteen, giving 42% of the British Pharmacopoeia analyses and forming the main group. Most of the 36% remaining are from the butanol–pyridine–nitropropane group, although trifluoropropyl–methyl polysiloxanes such as OV-210 are not used at all. Perhaps these phases and Apiezon L, should be uitilised?

REFERENCES

1 C. F. Poole and S. K. Poole, *Chem. Rev.*, 89 (1989) 377.
2 L. R. Snyder, *J. Chromatogr.*, 92 (1974) 223.
3 L. Rohrschneider, *J. Chromatogr.*, 22 (1966) 6.
4 W. O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
5 B. R. Kersten and C. F. Poole, *J. Chromatogr.*, 452 (1988) 191.
6 T. J. Betts, *J. Chromatogr.*, 354 (1986) 1.
7 *The British Pharmacopoeia*, Vol. I, Her Majesty's Stationery Office, London, 1988.