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METHOD FOR THE CLASSIFICATION AND SELECTION OF STATIONARY PHASES IN GAS CHROMATOGRAPHY

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SUMMARY

A new method of classification is applied to 233 stationary phases used in gas chromatography. Clustering together all those which have similar chromatographic behaviour, 45 are found to be singular in the sense that no other stationary phase exhibits similar characteristics and therefore they may not be replaced by any other. The remaining 188 stationary phases may be reduced to 33 selected liquids which may represent the larger set of 188, in the sense that all selectivity possibilities of the 188 stationary phases are retained in the 33 selected. A further reduction in the number of selected stationary phases will adversely affect the separation capacity of the set. The selected list of 33 stationary phases is not unique, and many of them may be replaced by an equivalent one without any loss in separation capacity.

INTRODUCTION

A very large number of substances have been used as stationary phases in gas chromatography and many of them have similar chromatographic characteristics. Hence characterization criteria that would allow comparisons between stationary phases and methods of reducing the number of those which should be used, through various methods of classification, are required. The most widely used method of characterization was proposed by McReynolds[1], who followed ideas previously presented by Rohrschneider[2,3]. McReynolds obtained retention indices for ten solutes at 120°C, then deduced the value of a constant or retention index increment by subtracting the corresponding retention index of the solute in squalane as a reference stationary phase.

However, there have been numerous attempts at classification[4–17] in which the stationary phases are gathered into groups so that each group could be represented by only one phase chosen for its better characteristics, such as thermal stability or higher maximum operating temperature. The general problem of all these methods and the classifications that they produce is that they tend to reduce the total number of stationary phases to too small a number of selected ones which, generally, cover a good range of "polarity", but do not substitute the selectivity of the larger set that

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they try to replace, *i.e.*, one often finds that a given separation normally carried out with a particular stationary phase cannot be performed by using the one that has been chosen as a substitute. In Wold's words[9]: "Clustering methods which force all phenomena (stationary phases) into clusters, force a non-existing similarity into the analysis".

In this paper, we try to give a real answer to a real problem, avoiding considering as similar stationary phases that do not behave similarly from a separation point of view. We have tried to reduce the number of stationary phases as much as possible, but without diminishing the separation capacity.

EXPERIMENTAL

Computations were carried out on a Control Data Cyber 180/855 computer.

Source of data

Initial data were the retention indices of the stationary phases published by McReynolds[1] with the exception of Triton X-400, which has a missing value, and the three following corrections[7]: constant value of 1,4-dioxane for Hallcomid M-18 OL, 111 instead of the reported 211; constant value of 2-octyne for Tergitol NPX, 139 instead of 39; and constant value of *cis*-hydrindane for CW 4000 monostearate, 145 instead of 45. To these 225 stationary phases we added those listed in Table I which have been characterized in our laboratory at 120°C using the ten McReynolds' solutes. The silicone OV-7 is included in Table I because our results differ considerably from those reported by McReynolds. Results corresponding to other methyl phenyl and cyanoalkyl silicone liquids agree fairly well with his results and therefore have not been included in Table I. Identification of stationary phases is made here with the help of a number (ID) which we have assigned to them. In McReynolds' table we assigned numbers to the stationary phases starting from No. 1 (squalane) and proceeding according to the consecutive order in which he presented them. Table II presents the IDs corresponding to a few stationary phases from McReynolds'

TABLE I

IDENTIFICATION NUMBERS (ID) FOR STATIONARY PHASES CHARACTERIZED IN OUR LABORATORY AT 120°C

Retention indices for OV-105: benzene, 688; *n*-butanol, 685; 2-pentanone, 712; 1-nitropropane, 781; pyridine, 778; 2-methyl-2-pentanol, 754; iodobutane, 844; 2-octyne, 875; 1,4-dioxane, 728; *cis*-hydrindane, 1011. For other retention indices, see ref. 18.

ID	*Stationary phase*
230	OV-7
239	OV-61
242	SP-2340
243	SP-2310
245	SP-2330
246	SP-2300
247	OV-275
251	OV-105

TABLE II

IDENTIFICATION NUMBERS FOR SOME STATIONARY PHASES

ID	*Stationary phase*
1	Squalane
25	SE-33
50	Octoil S
75	Dioctyl phthalate
100	Atpet 200
125	SAIB
150	Triton X-100
175	Quadrol
200	Butanediol succinate
225	Cyanoethyl sucrose

table. This table may serve as a guide to identify all others. Identification numbers for the stationary phases characterized in our laboratories are given in Table I.

Characterization procedure

The characterization procedure followed in this paper is simple. We use the retention indices of the ten McReynolds' solutes instead of the corresponding constants that he gave, thus eliminating the reference to squalane, which we considered irrelevant for our purpose. The characterization parameter is the retention index percentage contribution (*IP*) of each solute to the total sum of the ten retention indices corresponding to one stationary phase. The percentage contribution of the retention index of each solute on each stationary phase is calculated according to

$$IP_p^j = 100\, I_p^j \Big/ \sum_{p=1}^{10} I_p^j \tag{1}$$

where IP_p^j is the percentage contribution of the retention index; j refers to stationary phase j; p refers to probe p (each of the ten solutes used by McReynolds); I_p^j is the retention index of probe p on stationary phase j.

The main reason for choosing this parameter is that the selectivity of a stationary phase might not depend so much on the high or low values of the retention indices of the ten solutes as on their relative value. In other words, one cannot separate benzene from 2-pentanone on a stationary phase whose retention indices for those two substances are identical, no matter what the absolute value is. Two stationary phases are compared by comparing the *IP*s of every solute, and considering they have an equivalent *IP* for the solute only if both values agreed within a certain error. Only if *IP* values for a solute are equivalent is the *IP* value for the next solute taken for comparison. The two stationary phases are considered to be equivalent if all ten values of the *IP*s are equivalent. In this way, a mathematical compensation that would force non-existent similarities is avoided. The program compares in this way every stationary phase with all others.

In this paper, two *IP* values are taken as equivalent if they agree within 2%

TABLE III

RETENTION INDICES (RI) AND RETENTION INDEX UNITS CORRESPONDING TO A 2% ERROR (ε) FOR THREE STATIONARY PHASES

Solute	*Apiezon L*		*UCON LB-1715*		*CW 1450*	
	RI	ε	*RI*	ε	*RI*	ε
Benzene	685	14	785	16	1024	21
n-Butanol	612	12	887	18	1229	27
2-Pentanone	642	13	807	16	1080	22
1-Nitropropane	684	14	927	19	1318	26
Pyridine	741	15	934	19	1340	27
2-Methyl-2-pentanol	703	14	891	18	1169	23
1-Iodobutane	853	17	927	19	1143	23
2-Octyne	852	17	941	19	1096	22
1,4-Dioxane	685	14	853	17	1188	24
cis-Hydrindane	1039	21	1052	21	1178	24

of their value. For stationary phases j and k this happens if the following condition is fulfilled:

$$|IP_p^j - IP_p^k| \leqslant 0.02\, IP_p^j \tag{2}$$

This error represents a different number of retention index units, depending on the mean polarity of the stationary phase. Table III gives an idea of the magnitude of the errors for the ten solutes in three stationary phases of widely different polarity.

RESULTS

Graphical representation

The results of comparing each stationary phase with all others are presented in a graphical form in Fig. 1, which has been divided into five parts (a–e) for the sake of clarity. With this particular style of representation, those stationary phases which are similar gather together to form clusters, thus making a very intuitive representation of the corresponding classification. Every row and every column of the graphs represents one stationary phase identified by its ID on the axes. Horizontally distributed are the same phases, in the same order and with the same ID as those distributed vertically, although only some of the IDs are indicated as a guide. An × at the cross-over point of a row and a column of the graph corresponding to two stationary phases indicates that retention indices for the ten McReynolds solutes in these two phases correspond to equal IP values within a 2% error. It can be seen that the stationary phases are not quite in the order of their IDs, because the order was sometimes changed to make the clustering clearer.

The 233 stationary phases considered in this work may be said to belong to three different classes: (a) 154 stationary phases which gather together forming several large clusters; (b) 34 stationary phases which gather together in a similar way into small clusters (which we call "singular" groups) of only two or three similar phases;

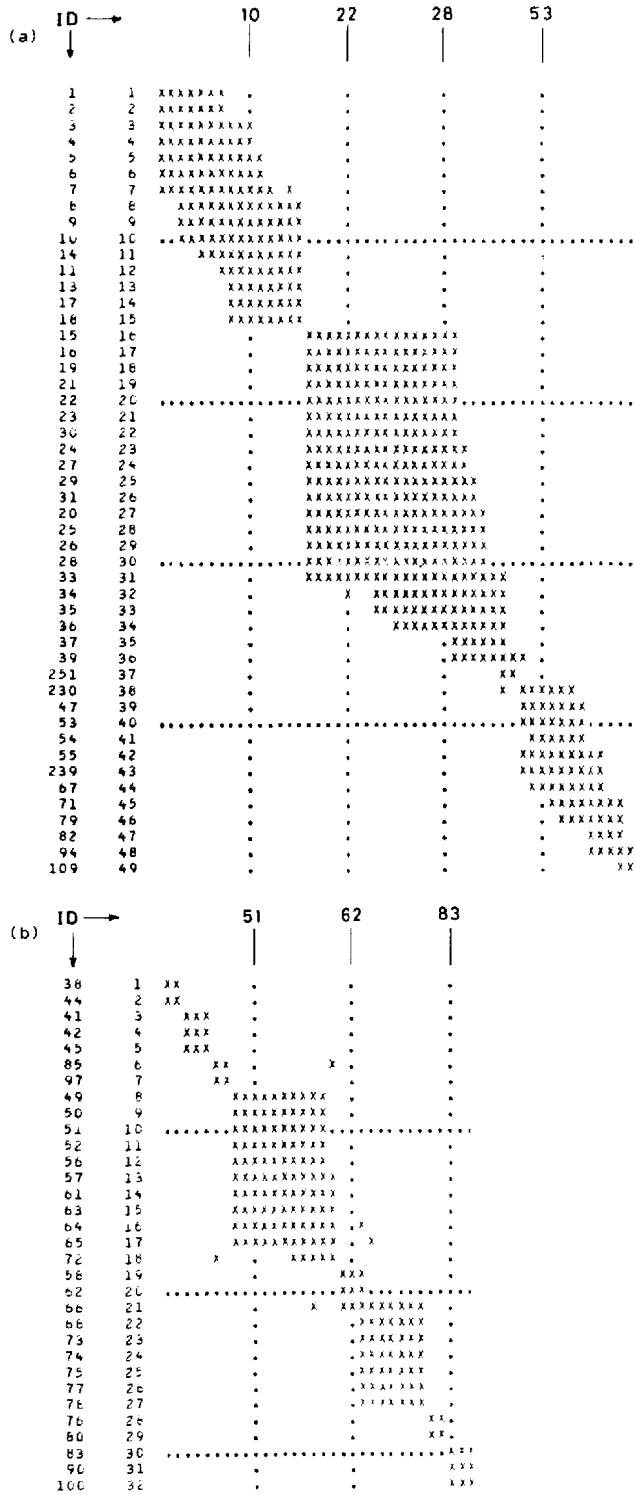
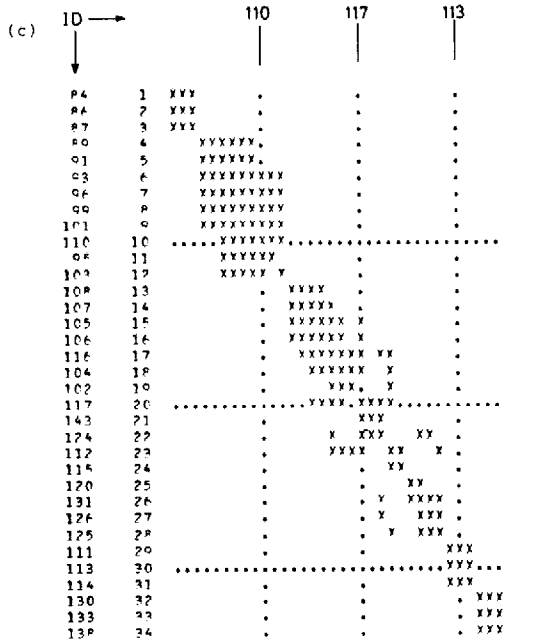


Fig. 1.

(Continued on p. 214)



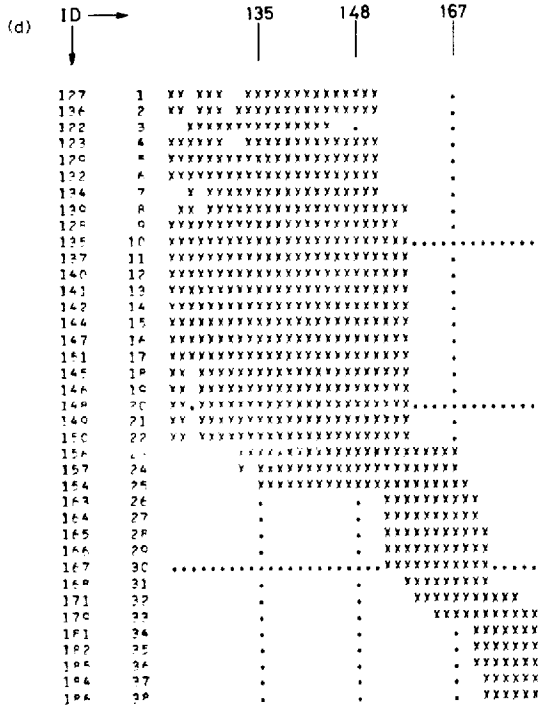


Fig. 1.

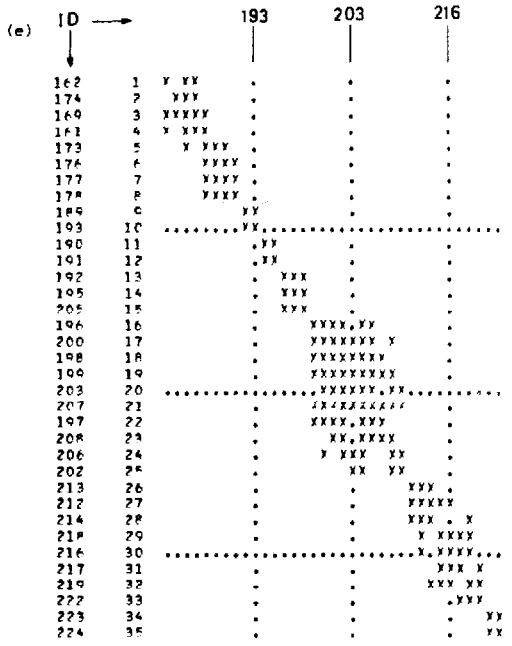


Fig. 1. (a–e) Graphical representation of similarities between stationary phases. An × at the cross-over point of two stationary phases means that these two phases are equivalent from a chromatographic point of view. First column: identification numbers (IDs) of the stationary phases. Second column: order in which phases appear in the graph. The figures have no other meaning. Stationary phases are plotted in the same order vertically and horizontally.

sometimes the small groups correspond to the same stationary phases from different suppliers; (c) 45 "singular" stationary phases that have no equivalent, *i.e.*, those phases whose selectivity characteristics are not found in any other of the 233 phases considered. Only phases of classes (a) and (b) are represented in Fig. 1; singular stationary phases are listed in Table IV.

Selection of stationary phases

Stationary phases that are equivalent (within a 2% error) behave similarly from a chromatographic point of view. Therefore, one stationary phase may be used instead of any of the phases which are equivalent to it. In this way, the former is said to represent all others, and may be selected to replace them. The aim of this section is to make a selection of stationary phases from Fig. 1 in such a way that a set of stationary phases can represent the 188 found in the figure. Each of the selected stationary phases should represent several others and the selection must be made so that all stationary phases are represented. The number of stationary phases selected should be the minimum necessary for the purpose.

The representation of the groups of similar phases by the clusters in Fig. 1 makes it easy to carry out the selection. To make use of Fig. 1, several general criteria should be taken into account. (a) If a cluster has the form of a square (with an equal number of rows and columns) and it is full of crosses (×) containing no gaps, any one of the stationary phases can represent the whole cluster. (b) If the cluster has

TABLE IV

SINGULAR STATIONARY PHASES

Key to abbreviations for several IDs: 59, bis(2-ethylhexyl) tetrachlorophthalate; 60, diethylene glycol stearate; 70, triethylhexyl phosphate; 118, tri(butoxyethyl) phosphate; 153, bis(2-ethoxyethyl) phthalate; 160, bis-ethoxy-ethoxyethyl phthalate; 170, cyclohexane dimethanol succinate; 187, ethylene glycol isophthalate; 201, phenyldiethanolamine succinate; 204, diethylene glycol adipate; 215, ethylene glycol phthalate; 221, tetracyanoethoxy pentaerytritol; 226, N,N-bis(2-cyanoethyl) formamide.

ID	*Stationary phase*	*Polarity index**	*ID*	*Stationary phase*	*Polarity index**	*ID*	*Stationary phase*	*Polarity index**
12	Montan wax	4	121	Squalene	33	201	PDEAS	65
32	DC-11	7	152	Stepan DS60	40	204	DEG adipate	66
40	Beeswax	10	153	Diethoxyet phth	40	209	Hyprose SP-80	70
43	Apiezon H	12	155	Siponate DS-10	41	210	ECNSS-M	76
46	OV-7 (McReynolds)	14	158	XE-60	42	211	Diglycerol	78
48	Apiezon W	15	159	OV-225	43	215	Et. glycol phthalate	82
59	Dietex tetracl phth	16	160	Bis (ethoethoet) phth	43	220	THEED	88
60	DEG stearate	17	170	CHDMS	48	221	Tetracyanoethoxy PE	89
70	Triethex phosphate	20	172	Zonyl D-7	49	225	Cyanoethyl sucrose	104
81	Flexol 8N8	23	175	Quadrol	50	226	BCEF	110
88	Zinc stearate	24	180	EGSP-Z	54	242	SP-2340	87
92	Castorwax	24	183	Epon 1001	55	243	SP-2310	76
98	Trimer acid	26	187	Et. glycol isophth	58	245	SP-2330	84
118	Tri(butoxyethyl)PO4	32	188	XF-1150	59	246	SP-2300	57
119	Zonyl E-91	32	194	MER 2	63	247	OV-275	100

* Polarity index: sum of the first five McReynolds' constants, taking as reference the value for OV-275 = 100.

any form other than a square and there are one or n rows full of crosses along the whole length of the row from the first column on the left to the last column on the right of the cluster, there are one or n possibilities, respectively, of replacing the whole cluster by one selected stationary phase; the selected row fulfilling the stated condition corresponds to the selected phase. (c) One may find that the cluster has some form other than a square and that condition (b) is not fulfilled, but that there are two rows covering together all the columns occupied in Fig. 1 by the cluster, from its first column on the left to its last column on the right. In such a case the two rows define the two stationary phases that together may replace the whole cluster. Overlapping of the two rows or gaps in any of them do not invalidate the criterion provided that the two rows do not have a gap in the same column. (d) The situation is the same as the preceding one, but there are more than two rows fulfilling criterion (c); then the number of possibilities of replacing the cluster by two selected phases is equal to the number of combinations of two rows among those fulfilling the above requirement. (e) The number, n, of selected phases necessary to replace the cluster increases, as does the minimum number of rows necessary to cover together all the columns occupied by the cluster with the conditions stated in (c). In this instance, the number of possibilities increases.

A selection of stationary phases representing large groups is presented as an example in Table V, where 20 phases offer the same separation possibilities as do the 154 phases which form large clusters in Fig. 1. If fewer phases were selected, part of the separation possibilities of the 154 phases would be lost. The selection, as can be deduced from the above criteria, is not unique. Only in one instance is the selected

TABLE V

STATIONARY PHASES REPRESENTING LARGE GROUPS

ID	*Stationary phase*	*Polarity index**
1	Squalane	0
9	Apiezon L	3
28	OV-101	5
39	OV-3	10
230	OV-7	14
79	OV-17	21
109	OV-25	28
65	Diisodecyl adipate	17
66	Diisodecyl phthalate	18
101	UCON LB 1715	27
106	Didecyl phthalate	27
112	Tributyl citrate	29
124	Tricresyl phosphate	34
137	Igepal CO-630	37
165	Igepal CO-880	46
181	Carbowax 20M	55
169	HI EFF 8 BP	48
207	LAC-2-R 446	67
212	Diethylene glycol succinate	78
222	Ethylene glycol succinate	89

* See Table IV.

TABLE VI

STATIONARY PHASES REPRESENTING SMALL SINGULAR GROUPS

ID	*Stationary phase*	*Polarity index**
44	Butoxyethyl stearate	12
42	Kel-F-Wax	12
85	Hercoflex 600	23
80	Hallcomid M-18 OL	22
86	Versamid 930	23
90	Span 80	24
114	OS-138	30
133	OV-210	36
177	Neopentyl glycol succinate	50
193	Sucrose octaacetate	62
190	FFAP	60
205	Carbowax 1540	66
223	1,2,3-Tris(cyanoethoxy)propane	98

* See Table IV.

stationary phase the only one that meets the requirements of representing a large group of phases. We refer to stationary phase 207, LAC-2-R-446, which can replace a group of ten stationary phases similar to one another within a 2% error (Fig. 1e). Any other stationary phase would represent part of the group but would never represent all of them, so two stationary phases would have to be selected if phase 207 was not chosen. In all other instances, a different stationary phase would give the same result of truly representing as many phases as does the selected stationary phase from the list in Table V. Let us consider stationary phase 101 (Ucon LB 1715). In this instance (Fig. 1c), one of the stationary phases 93 (Flexol B-400), 96 (PPG 2000) and 99 (Pluracol P2010) would produce the same results. Similarly, all other selected phases in Table V could be replaced by a different one. Hence, the selection is not unique, but the number of twenty selected phases cannot be reduced without a corresponding reduction in selectivity.

The number of stationary phases that form small groups of two or three stationary phases is 34, and they are represented by the list shown in Table VI, a total of thirteen phases. As with large groups, other stationary phases could have been selected instead, but thirteen is the minimum number that must be selected in order to retain the separation of the 34 phases. The clusters here are very well defined, except for the two groups of stationary phases represented by phases 85 and 177. In both instances, one of the phases forming the group shows similarities with one or more phases from a nearby group, indicating that the variation of chromatographic characteristics of the phases is gradual. A larger error (say 2.5 or 3%) would produce the effect of integrating such groups to form a single larger group, but in that instance the similarity between stationary phases would correspond to a difference of more retention index units.

Summing up all the above considerations, the 188 stationary phases represented in Fig. 1 can be reduced to a set of 33 phases without any loss of separation capacity. This means that any separation carried out with any of the 188 phases can be performed with a suitable phase chosen from the set of 33 included in Tables V

and VI, if allowance is made for the 2% error used in the comparison. The importance of the 2% error may be deduced from Table III. Bearing in mind that two stationary phases are similar only if they behave similarly with a number of solutes, a reduction in the number of selected stationary phases in the list would represent a reduction in the overall separation capacity.

The classification and selection method presented here differs in three respects from the results offered by other workers: (a) it selects a larger number of stationary phases as the minimum, which cannot be reduced further without a loss in overall separation capacity; (b) there are more clusters of similar phases, clusters which are definitely different from one another; (c) there is a larger number of singular phases, that is, phases which have no other equivalent. These three differences arise because the method presented here is more stringent, *i.e.*, the *IP* values used as characterization parameters are separately compared one by one, in such a way that there cannot be any possible mathematical compensation among them, a compensation that was not usually avoided in former classification methods.

We are aware of two limitations. The first is that some of the 78 stationary phases selected are obsolete and it may be necessary to delete them from the list; in doing so, it is certain that, if no other similar new phase can be found, part of the separation capacity will be lost. The second limitation is that some new stationary phases are not included in this study because there are not enough available data on the values of the ten McReynolds constants, five or sometimes seven values normally being reported. However, the main purpose of this work was not so much to make a complete selection from all commercial stationary phases (which may be carried out in the future) as to present a method of selection that preserves the separation capacity of the stationary phases involved in the selection process.

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