

CHROM. 10,241

## GAS CHROMATOGRAPHIC SEPARATION OF ALL C<sub>1</sub>-C<sub>4</sub> HYDROCARBONS BY MULTI-SUBSTRATE GAS-SOLID-LIQUID CHROMATOGRAPHY

W. K. AL-THAMIR, R. J. LAUB and J. H. PURNELL

*Department of Chemistry, University College of Swansea, Swansea, Wales (Great Britain)*

---

### SUMMARY

The feasibility of developing a single column capable of the isothermal separation of all 32 C<sub>1</sub>-C<sub>4</sub> hydrocarbons in a single analysis is discussed. It is shown that such a master column can be devised either via the gas-solid chromatographic (GSC) or the gas-solid-liquid chromatographic (GSLC) techniques. The advantages of the latter are demonstrated. An experimental study has revealed that prior exposure to simple volatile liquids has a remarkable effect on the retention behaviour of both alumina and alumina heavily coated with involatile liquid. It is established also that GSLC can provide a superior solution to analytical problems than can either GSC or gas-liquid chromatography. Finally, it is shown that, when mixed liquids are used in GSLC, the liquid mixture compositions can be quantitatively predicted via a strategy developed previously by the authors.

---

### INTRODUCTION

The chromatographic separation of all the C<sub>1</sub>-C<sub>4</sub> hydrocarbons in a single isothermal analysis is not, contrary to belief, simply achieved. The reasons are straightforward. Not only do the thirty or so compounds involved represent a wide range of chemical types including all levels of unsaturation, as well as cyclics, but also the boiling range exceeds 200°. This and the extremely low boiling points of most of the earlier members mean that adequate resolution of the earlier members leads to very lengthy retention of higher members. Conversely, acceptable retention times for the latter generally correspond to such small capacity factors for the lower members that column efficiencies are usually inadequate to provide their separation. The problem is particularly severe in gas-liquid chromatography (GLC) since, at convenient analysis temperatures (*e.g.* ≥0°), partition coefficients of the first half-dozen compounds are small and, so far, solvents of sufficient selectivity to offer easy separation of all four butenes, or of ethyne, propadiene, propene and cyclopropane are few. This matter is elaborated later. In contrast, in gas-solid chromatography (GSC), not only are partition coefficients greater, but also considerable and more varied selectivity is observed. Thus, in principle, it should be more readily possible to devise a GSC than a GLC system that can provide, in a single run, resolution of all C<sub>1</sub>-C<sub>4</sub> compounds. There are, however, two difficulties to overcome. First, GSC analysis times are likely

to be enormous and, secondly, unacceptable peak asymmetry or generally low theoretical plate efficiency is likely to be experienced.

Except in a few instances, the broad problem that we have defined has been solved in the past by a combinatory approach based on multiple column analysis involving GSC, GLC or complexing substrates and/or temperature programming. We are not aware of any single-column isothermal GLC solution, except for the simplest of mixtures.

We recognize that all the compounds in the group will rarely, if ever, occur in a given mixture. But it is clearly essential in designing the requisite analysis to know which are present. This brings us to the concept of a master column, *i.e.* a column that will separate all possible components of a given group of compounds and, on this account, not only will allow reasonably secure identification via retention coincidence but also easy back-up confirmation by gas chromatography-mass spectrometry or other ancillary techniques. Such a column would perhaps only be occasionally used since, once mixture identities were established, the optimization strategy described by us elsewhere<sup>1-4</sup> could be brought to bear, and an entirely different column would be indicated for any given separation.

With this in mind, and in the light of our earlier considerations, we have initiated a study designed to produce a convenient master column. We have based our approach on the gas-solid-liquid chromatographic (GSLC) method, *i.e.* one in which an involatile liquid is distributed on an active solid. We choose this approach, first, because it has been for many years the method of choice in this laboratory in the analysis of the only moderately complex mixtures of C<sub>1</sub>-C<sub>4</sub> arising in gas kinetic studies and, secondly, and in particular, because of the very comprehensive and encouraging work of Paterok and his colleagues<sup>5,6</sup>. These authors have studied the effect of liquid identity and loading on the performance of a variety of aluminas and have ascertained conditions in which seventeen of the C<sub>1</sub>-C<sub>4</sub> hydrocarbons are almost completely resolved at 20° with a column of alumina coated with 1,2,3-tris(2'-cyanoethoxy)propane. This study concentrated on the use of highly polar liquids and, with little exception, very high liquid loadings running up in excess of 30% (w/w). In our view, very much smaller liquid loads are likely to be more effective, and, further, we see no reason why any liquid at all should not offer prospects of success. Finally, we have, in the course of our experience, observed irreproducibilities which indicate the possibility that the choice of volatile solvent used to introduce the involatile liquid may be important.

Since the problem has never been satisfactorily resolved, and since it seems to us that the most appropriate approach is via GSLC, we have commenced on a broad study designed to establish in greater detail than exists now, first, the scope of the technique and, secondly, the most useful approach to the evaluation of optimizing criteria.

## EXPERIMENTAL

The experiments were conducted using a precision chromatograph constructed in the laboratory. For the GLC experiments, columns were made up using 120-140 mesh silanized Chromosorb G as support, the packing being contained in a 1.3 mm I.D. stainless-steel tube. For the GSC and GSLC experiments, the active solid was

alumina (Alcoa F 20). It was found that acid-washed varieties gave rise to such peak asymmetry and low theoretical plate efficiency that, in spite of a certain degree of selectivity, they were virtually unusable. The water-washed variety, in decided contrast, yielded symmetrical peaks and much greater selectivity. A 100-120 mesh fraction of this was, therefore, used throughout the work, again in stainless-steel columns of 1.3 mm I.D. The efficiency of such columns was only about 300 theoretical plates per foot, *i.e.* well below that attainable in GLC, but is adequate for our present purposes.

Prior to use, the alumina was dried in a vacuum oven at 145° for not less than two days. Coated alumina samples were dried for 2 h at 110° to remove volatile solvent. The packed column was then conditioned *in situ* in the chromatograph until a perfect baseline was obtained at minimum detector attenuation.

Of the 32 hydrocarbons within the C<sub>1</sub>-C<sub>4</sub> group, a half-dozen or so are so thermally unstable that they need not be considered in the context of gas chromatography at temperatures above room temperature. Six others are unobtainable from normal sources and must be synthesised. Of the remaining twenty available to us, cyclobutane and the three butynes were in such short supply that they were used only occasionally. This presents no problem since the butynes are easily separable from each other and all other components. Hence, we do not include them in the chromatograms illustrated. Cyclobutane too offers little difficulty in separation from butenes and butanes and so, was also normally excluded.

#### Gas-liquid chromatography

A comprehensive literature search reveals that no more than a half-dozen or so liquids are widely used for C<sub>1</sub>-C<sub>4</sub> analysis by GLC. Although some quite dramatic shifts in relative retention are seen from one liquid to another, in practice it is found virtually impossible to achieve complete resolution of even a limited number of components in a single isothermal run. We illustrate the problem with the data of Table I.

TABLE I  
RELATIVE RETENTION DATA FOR C<sub>1</sub>-C<sub>4</sub> HYDROCARBONS, GLC AT 0°

No.	Hydrocarbon	$\alpha$			
		Squalane	DNP	DBM	ODPN, 2% (w/w)
1	Methane	0.048	0.056	0.070	0.072
2	Ethene	0.202	0.275	0.353	1.07
3	Ethane	0.218	0.230	0.262	0.270
4	Ethyne	1.18	0.512	1.08	6.29
5	Propene	0.863	1.12	1.28	2.64
6	Propane	1.00	1.00	1.00	1.00
7	Propyne	1.08	3.21	5.28	26.4
8	Propadiene	1.33	2.45	3.16	9.58
9	Cyclopropane	1.94	2.58	2.75	6.01
10	1-Butene	3.67	4.44	4.69	6.59
11	Isobutene	3.52	4.55	4.81	7.07
12	<i>trans</i> -2-Butene	5.03	6.16	6.29	8.32
13	<i>cis</i> -2-Butene	5.76	7.16	7.36	10.10
14	<i>n</i> -Butane	4.52	4.25	3.74	3.95
15	Isobutane	2.57	2.57	2.33	2.24
	$K_R$ (propane)*	15.3	11.5	11.8	1.67
16	1,3-Butadiene	—	—	—	—

\*  $K_R$  = liquid/gas partition coefficient.

Here are listed relative retention ( $\alpha$ ) data for four commonly used liquids for the fifteen most commonly encountered hydrocarbons of this group. The data relate to elution at 0° because, at this temperature, the relevant values of  $\alpha$  are most favourable; for  $\beta, \beta'$ -oxydipropionitrile (ODPN), the data relate to a 2% (w/w) column and are not independent of liquid loading in contrast to the other data cited. The agreement between our data and the few published is very good.

In terms of minimum  $\alpha$ , the most difficult separation on squalane is that of 1-butene and isobutene for which  $\alpha = 1.043$ . If we constructed a column of capacity factor ( $k'$ ) = 10 for 1-butene, we would require 25,600 theoretical plates for complete resolution of this pair. This is not too demanding, it would seem. However, the corresponding  $k'$  for ethane would then be so small that we would require 48,000 theoretical plates to achieve separation of ethane and ethene. Further, in order to achieve such values of  $k'$  we would need a solvent loading of over 60% (w/w), at which point the column efficiency would be so diminished that an astonishing column length would be required for separation.

Dinonyl phthalate (DNP) presents an even worse situation since the separation of cyclopropane and isobutane ( $\alpha = 1.004$ ) demands  $3 \times 10^6$  theoretical plates. Di-*n*-butyl maleate (DBM) offers a somewhat better prospect in that the most difficult separation in terms of  $\alpha$ , again that of 1-butene and isobutene ( $\alpha = 1.026$ ), is also the most difficult if  $k'$  for isobutene = 10, and demands 67,800 theoretical plates. However, to achieve such a  $k'$  value the column would need to contain around 55% (w/w) of the liquid and, clearly, a column many hundreds of feet long would have to be employed.

Finally, ODPN superficially offers a very acceptable solution since the most difficult separation, that of ethyne and 1-butene ( $\alpha = 1.048$ ), requires only 20,800 theoretical plates at  $k' = 10$  for 1-butene. However, a 25% (w/w) column would be needed. It is well known that ODPN owes much of its solvent power and selectivity to the participation of liquid surface adsorption, hence the loading dependence of retention. At loadings in the region of 20%, in fact, all the major selectivity of ODPN for the compounds of interest disappears. Thus, the notional separation cannot in practice be achieved.

Since the most difficult pair to separate with ODPN is not the same as that for squalane, for example, it might be thought possible to find a mixture of the two packings that would be better than either alone. In fact, since, as can be seen from Table I, there is retention inversion of 1-butene and isobutene on going from squalane to ODPN, there is no mixture that is better than ODPN alone.

The foregoing illustrates in quantitative terms the qualitative practical experience of those mainly interested in C<sub>1</sub>-C<sub>4</sub> analysis, that is, failure to find an adequate GLC column even when, in principle, one should be available. It is for this reason that we have concluded that further search via GLC is probably futile.

### *Gas-solid chromatography*

Preliminary experiments indicated that the selectivity of the alumina was such that complete resolution of all nineteen sample components could be achieved with a column providing around 6000 theoretical plates. This demanded a length of about 22 ft. (670 cm). We thus, in all the work reported from here on, standardized on this length. Fig. 1a illustrates the separation of the standard sixteen compounds. The

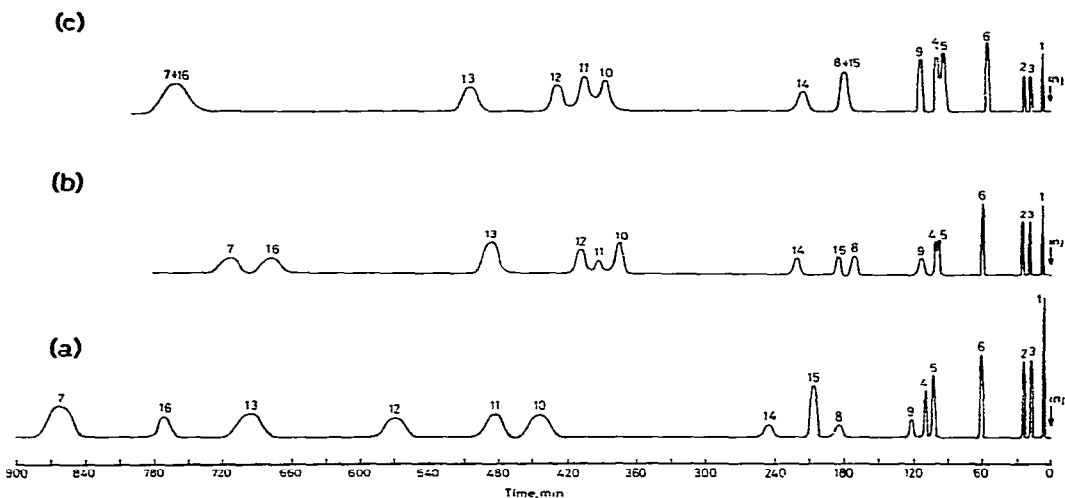


Fig. 1. Chromatograms obtained with 22-ft. long columns of F 20 alumina at 50°, (a) untreated, (b) benzene-washed and (c) *n*-hexane-washed. Peak numbers refer to the compounds listed in Table I.

analysis time is over 15 h and would be vastly greater if the butynes were included. Clearly, there is much room for improvement even though there can be little doubt that a master column can be based on this alumina.

Before proceeding to the GLSC work it appeared to us to be prudent to ascertain what effect washing of the alumina with volatile solvent might have. The basis for this precaution has been indicated, and it is seen to be realistic if only on account of the evident high adsorptive capacity of the alumina, its known catalytic activity and the practical need to introduce high-boiling GLC liquids via solution in volatile solvents. An illustration of the results of this study is contained in the chromatograms of Fig. 1. First, overall retention is clearly reduced by the preliminary wash with both liquids. Secondly, the effect in detail depends on the identity of the wash liquid since there are differences in selectivity to be seen in the various chromatograms. For example, following the benzene wash, separation of the C<sub>4</sub> alkenes is much reduced while acetylene and propene are only barely resolved. Similarly, following the *n*-hexane wash, both the C<sub>4</sub> alkenes and ethyne and propene are poorly resolved while, in addition, allene and isobutane and propyne and 1,3-butadiene are not resolved at all. Thus, perhaps surprisingly, we see that exposure of the alumina to *n*-hexane has a far more deleterious effect than has exposure to benzene. Clearly, in view of the relatively inert nature of these solvents, this implies that almost any liquid will have some effect and that this is as likely to be advantageous as disadvantageous.

So far as we have been able to determine, the effects are permanent insofar as the washed packings were subject to protracted heating at a temperature well above the relevant boiling point before the columns were packed and each column was conditioned for at least 12 h, and usually longer, in the chromatograph before use. Subsequent use involved many hours running and no retention time changes were noted.

No attempt has yet been made to characterize the nature of the treated alumina beyond determining that at very high temperature a high-boiling liquid can be eluted from an acetone-washed column. This, as might have been expected, implies chemical reaction over and above any chemisorption on the alumina, which suggests a fertile area for research in GSC solid modification, particularly since it may provide a means of depositing very thin films of involatile liquid.

### *Gas-solid-liquid chromatography*

The foregoing indicates that we must, before proceeding farther, check the effect of the use of alternative volatile solvents in laying down a given GLC liquid since there is no reason to assume that the effect of the volatile solvent will be eliminated by the deposition of the involatile liquid. Fig. 2 illustrates the chromatograms obtained with alumina coated with 1% (w/w) squalane deposited from either *n*-hexane or benzene. We see that the separation of isobutene and *trans*-2-butene and that of allene and isobutane are substantially better where *n*-hexane has been used. This comparative behaviour is in complete contrast to that described above and could obviously not have been predicted. Clearly then, choice of volatile solvent is important in GSLC. This aspect is brought out even more clearly in Fig. 3, which illustrates the chromatograms obtained with columns of alumina coated with 5% (w/w) squalane. The squalane had been, variously, introduced from solution in acetyl acetone (a),

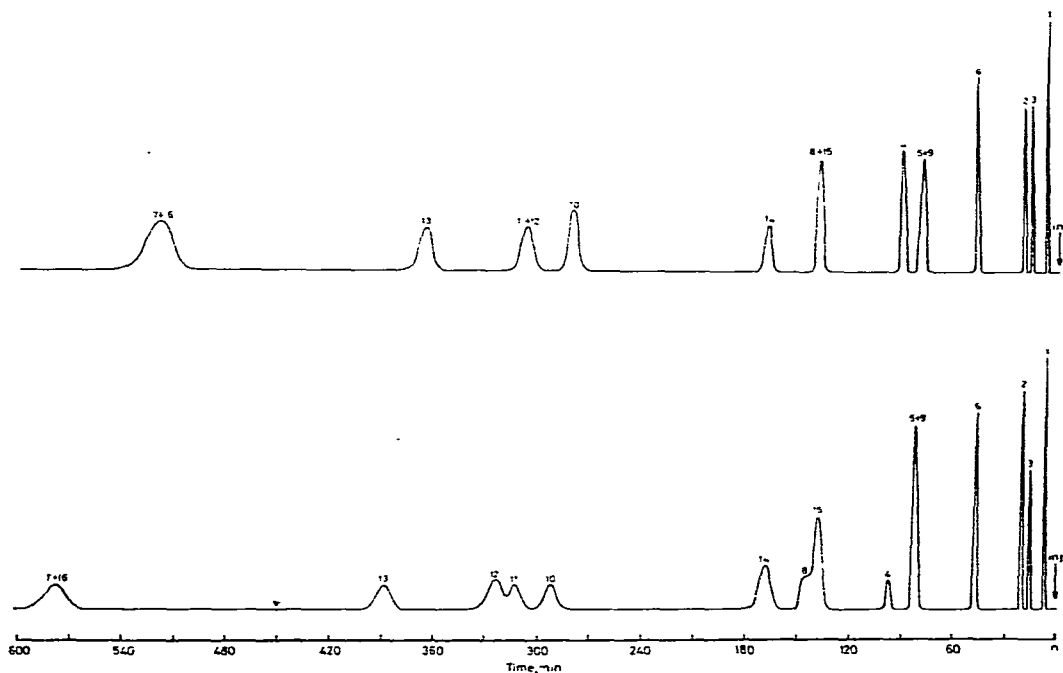


Fig. 2. Chromatograms obtained with 22-ft. long columns of 1% (w/w) squalane deposited on F 20 alumina from benzene (upper figure) and *n*-hexane (lower figure). Column temperature, 50°. Peak numbers refer to the compounds listed in Table I.

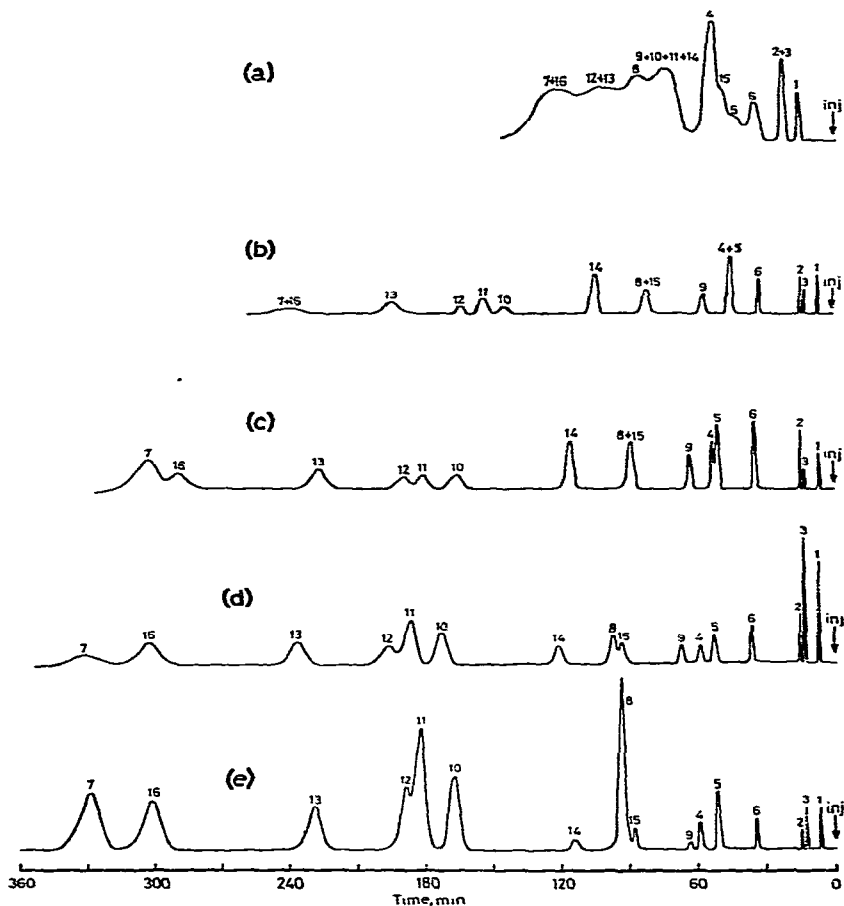


Fig. 3. Chromatograms obtained with 22-ft. long columns of 5% (w/w) squalane deposited on F 20 alumina from (a) acetyl acetone, (b) acetone, (c) furan, (d) thiophene and (e) benzene. Column temperature, 50°. Peak numbers refer to the compounds listed in Table I.

acetone (b), furan (c), thiophene (d) and benzene (e), respectively. The effects are dramatic. In chromatogram (a) there is, to all intents and purposes, no separation at all. In chromatogram (b), three pairs overlap exactly. In chromatogram (c), one pair overlaps exactly and two others are only partially resolved. In chromatograms (d) and (e), which are not too dissimilar in spite of the substantial difference in nature of the solvents, there is near complete resolution with only two pairs partially resolved. Even at heavy loadings an effect of the volatile solvent shows through very strongly.

It is, thus, firmly established that the choice of volatile solvent is crucial in determining the effectiveness of GSLC, a fact we believe never to have been established conclusively before although it may well have been implicit in reports of irreproducibility of GSLC data.

We turn now to the effect of change of GLC liquid substrate. Fig. 4 illustrates the chromatograms obtained with columns of alumina with 5% (w/w) of, respectively,

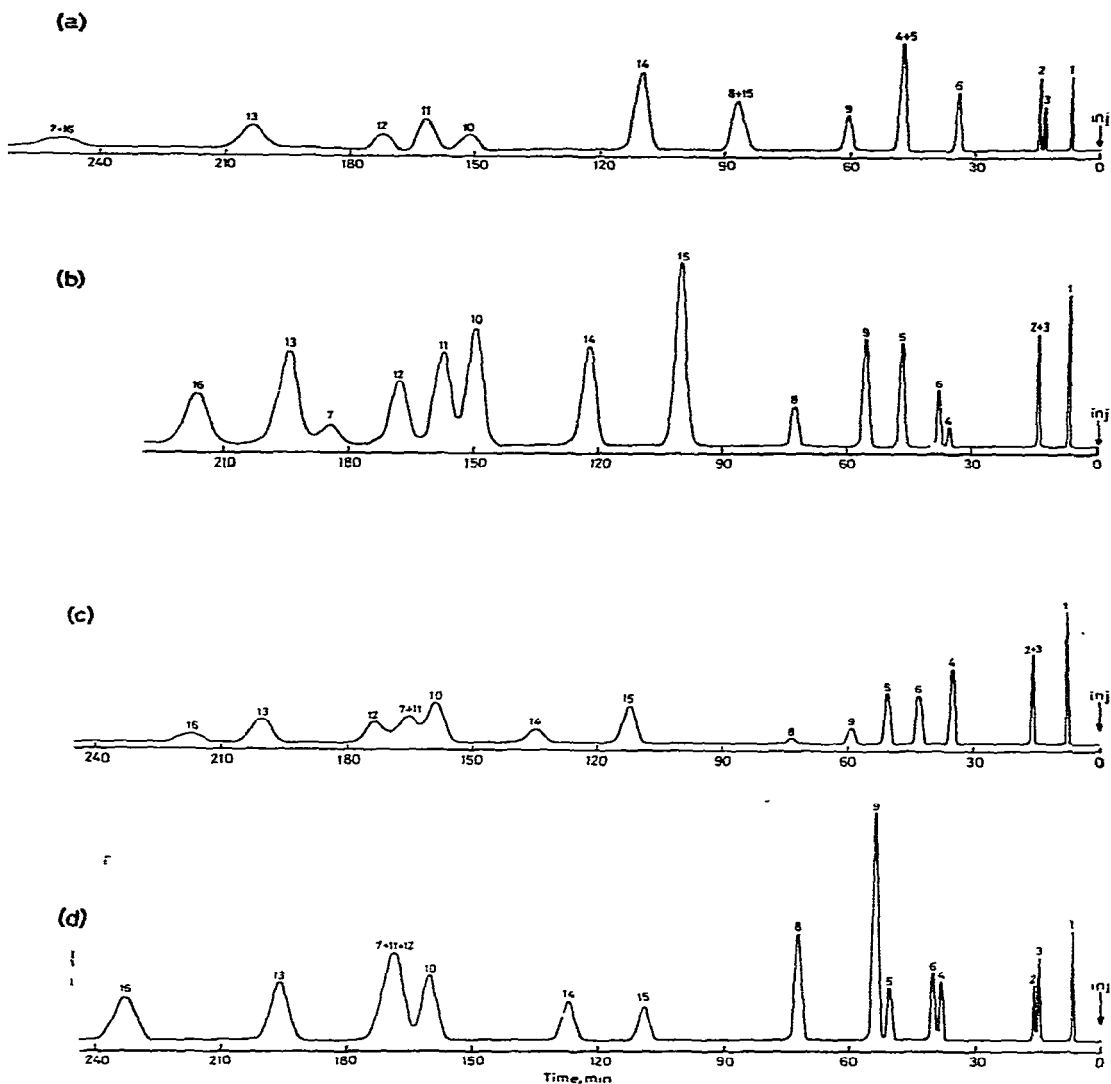


Fig. 4. Chromatograms obtained with 22-ft. long columns of 5% (w/w) involatile liquid acetone deposited on F 20 alumina at 50°. (a) squalane, (b) DNP, (c) DBM and (d) ODPN. Peak numbers refer to the compounds listed in Table I.

squalane, DNP, DBM and ODPN. All were introduced to the alumina in acetone solution. As would be expected, we see substantial variation from one to the other. Both DBM and DNP provide generally better separation than does squalane except that neither allows any resolution at all of ethane and ethene. Thus, no one of these three liquids provides the prospect of a complete solution. ODPN presents an even less promising prospect since isobutene, *trans*-2-butene and propyne are exactly coincident, a disappointing feature in view of the fact that all other components are remarkably well separated. Because of the identity of the coincident components we



see also that neither a series column nor intimate mixture with one of the other three packings is likely to provide a convenient solution.

Returning to the case of the first three liquids we see that, since their individual failures in separation relate to different sample pairs, it should be possible to use some combination of these liquid substrates to achieve the desired result. We have applied our optimum window technique<sup>1-4</sup> to the data for DNP and squalane and this indicated a requirement for a solvent coating containing squalane at a volume fraction of 0.60. However, it also specified a minimum value of  $\alpha$  (most difficult pair to separate) corresponding to a number of theoretical plates well in excess of what could be achieved with a 22-ft. column of these coated aluminas. With this length we would then expect only partial resolution of ethane and ethene and of propyne and *cis*-2-butene. Fig. 5 illustrates the chromatogram obtained, which is obviously very much in accord with prediction. Thus, we have established that liquid mixtures may be used, on a predictive basis, in GSLC. We see from Fig. 5 that the use of a longer column, one capable of providing about 9000 theoretical plates (*ca.* 33 ft.) would, in fact, have given complete resolution.

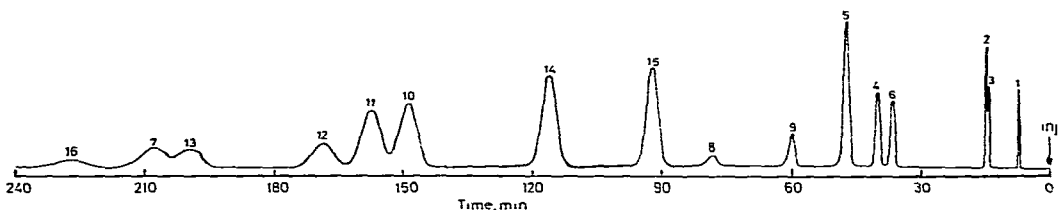


Fig. 5. Chromatogram obtained at 50° with 22-ft. long column of a mixture of DNP and squalane packings of Fig. 4 of volume fraction of squalane,  $\phi_s = 0.6$ , the composition predicted to give optimum separation at this column length. Peak numbers refer to the compounds listed in Table I.

We turn finally to the question posed originally, namely can GSLC provide a better answer than either GSC or GLC alone. There is no question, from any point of view that, for such mixtures as are dealt with here, it offers much advantage over GLC. Since we chose as the base for this work a GSC column of untreated alumina that could provide a solution it now remains to be established whether our results so far can answer the question with respect to GSC.

Our approach to this has been to study the effect of liquid loading and we have chosen to use, as our example, columns of benzene-washed alumina with squalane coating since this is not obviously the most promising system.

Before proceeding farther it is worthwhile to define the word "better" in the present context since, in chromatographic circles, interpretation of better is to some extent a subjective matter. Thus, for example, different workers may regard better as meaning faster analysis, or shorter columns, or the need for only low inlet gas pressures, or higher resolution, to mention only four of the available alternatives. Here, we settle for greater separation in shorter time.

Rather than present the chromatograms for packings of alumina loaded with squalane of up to 10% (w/w), we have chosen to identify the eight sample pairs which present difficulty of separation at one or other loading and, in Fig. 6, we plot the relative retention data for each pair against the percentage (w/w) of squalane. It is im-

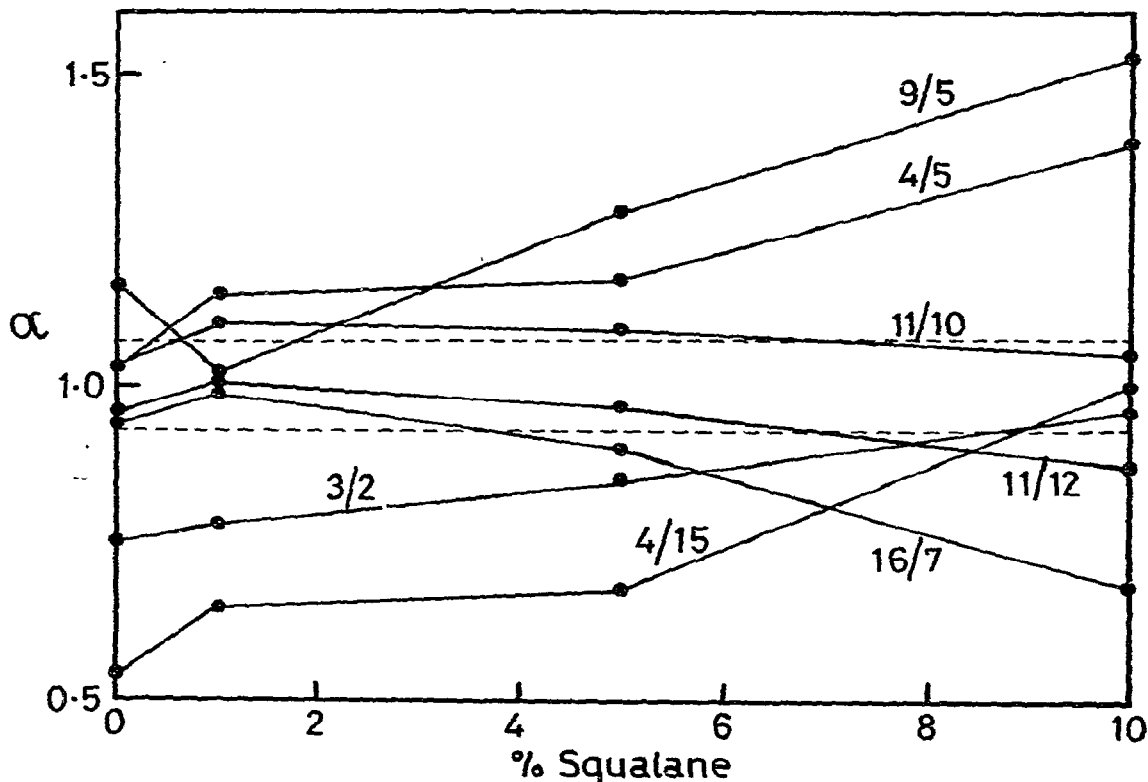


Fig. 6. Plots of  $\alpha$  for pairs of compounds difficult to separate against % (w/w) of squalane on benzene washed F 20 alumina. Elution at 50°.

mediately clear that retention behaviour is discontinuous as a function of squalane load. Since no simple interpolation procedure can, in consequence, be satisfactory, we thus adopt an alternative. The efficiency of our 22-ft. column allows separation of any pair of  $\alpha \geq 1.09$ . If, thus, we look along the figure within the region  $\alpha = 0.91$  to 1.09 we can determine the number of incompletely resolved pairs resulting from use of any column with squalane in the range 0 to 10% (w/w) simply by counting the number of lines that appear within the band. The minimum number clearly occurs at a finite amount of squalane. If, now, we look within closer limits we see that within the band  $\alpha = 0.93$  to 1.07, there are, in principle, no unresolved pairs at 7.25% (w/w) squalane, that is, this band is clear of lines. Thus, we may test the hypothesis by constructing a column of this composition providing about 9000 theoretical plates (the requirement for separation at  $\alpha = 1.07$  at high  $k'$ ), *i.e.* around 33 ft. long. Fig. 7 shows the chromatogram obtained.

Our prediction is clearly borne out since, with the exception of a small overlap of *trans*-2-butene and cyclobutane, resolution is fully achieved. We recognize that the time of analysis is lengthy but this is no particular handicap in the context of the master column concept. Further, there are clearly potential means for speeding up the analysis, *e.g.* higher temperatures and improved intrinsic column efficiency.

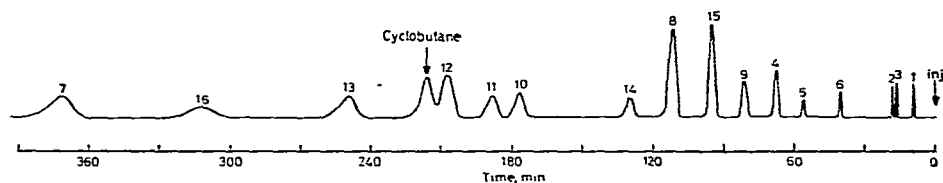


Fig. 7. Complete separation of 17 most common C<sub>1</sub>-C<sub>4</sub> hydrocarbons at 50° on 33-ft. long column of 7.25% (w/w) squalane benzene deposited on F 20 alumina. Column composition and length as deduced from Fig. 6. Peak numbers refer to the compounds listed in Table I.

Finally, it is obviously possible that some other involatile liquid may well offer substantial improvement since squalane is hardly to be regarded as the most probable optimum.

## DISCUSSION

The results presented here appear to us to confirm the promise of the GSLC technique implied in the relatively sparse literature on the subject. Perhaps the most attractive aspect is the remarkable flexibility available in the search for selectivity since we have identified at least four variables extra to those normal to GSC or GLC: (a) choice of active solid; (b) pretreatment with volatile liquids; (c) choice of involatile liquid; and (d) the combination of involatile liquids. Further, as has been shown, a quantitative approach to optimization of (c) and (d) is available.

The results, although only preliminary, also establish two other important points. First, it is clear that more or less any liquid can be employed with reasonable prospect of success. Indeed, given a sufficiently long column, with optimized loading, it seems as though any one of the systems we have studied could provide a solution to the current problem. Secondly, it seems that liquid loadings somewhat lower than have generally been used before will prove most useful. Presumably, this is because, with increasing loading, column performance approaches that of the corresponding GLC column.

In the light of the foregoing we would expect a widening of interest in the use of GSLC since there is no obvious reason why it should not be equally successful in the analysis of other sample types and since, also, our work has indicated some of the possible origins of the irreproducibility and poor performance that have, from time to time, caused concern. Given only now that means can be devised to achieve column efficiencies such as we normally obtain in GLC, *ca.* 800-1000 theoretical plates per foot, we see no reason why GSLC should not challenge GLC as the dominant gas chromatographic technique.

As regards the C<sub>1</sub>-C<sub>4</sub> separation, there can be no doubt that a master column can be devised. Indeed, we anticipate that many alternative columns, each capable of providing complete resolution, can be defined and the issue is then to choose the best. We plan to illustrate this point and to do so in a study involving all stable compounds in the group.

## REFERENCES

- 1 R. J. Laub and J. H. Purnell, *J. Chromatogr.*, 112 (1975) 71.
- 2 R. J. Laub and J. H. Purnell, *Anal. Chem.*, 48 (1976) 799.
- 3 R. J. Laub and J. H. Purnell, *Anal. Chem.*, 48 (1976) 1720.
- 4 R. J. Laub, J. H. Purnell and P. S. Williams, *J. Chromatogr.*, 134 (1977) 249.
- 5 N. Paterok and E. Wandsik, *Chem. Anal.*, 15 (1970) 977.
- 6 N. Paterok and W. Kotowski, *Chem. Anal.*, 16 (1971) 801.