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ENHANCEMENT OF GAS-SOLID CHROMATOGRAPHIC COLUMN PERFORMANCE BY INERT SOLID DILUTION

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SUMMARY

Column packings comprising an active solid sorbent diluted with an appropriately chosen inert, diluent solid have extremely desirable chromatographic characteristics. Theoretical plate heights can be substantially reduced in gas-solid chromatography (GSC) and at least maintained in gas-solid-liquid chromatography (GSLC) or high-performance liquid chromatography. Of greater importance, total analysis times can be reduced to any desired extent without loss of efficiency, and often with gain. Reduced analysis time can be traded-off for operation at lower temperature, a valuable option where samples are thermally labile or subject to catalytic reaction. Examples of difficult C_1 - C_4 aliphatic hydrocarbon analyses, both by GSC and GSLC, are given and it is concluded that the inert dilution technique provides a viable route to the extension of these modes of chromatography to a wider range of sample types than is currently common.

INTRODUCTION

Gas-solid chromatography (GSC) has found use almost exclusively in the analyses of permanent gas and low molecular weight aliphatic hydrocarbon mixtures. The reasons are twofold. First, adsorption of most other compounds is so strong that retentions are over-long except at very high temperature. One is thus faced with the choice of using short columns at moderate temperatures, and thus achieving little resolution, or of using longer, more efficient columns at high temperatures, which introduces the considerable risk of catalytic column reactions. Secondly, the variety of gas-solid adsorption isotherms likely to be encountered and the relatively slow mass transfer through porous adsorptive particles can lead to both poor (large) theoretical plate heights and, frequently, substantial peak asymmetry. GSC, and its variant gas-solid-liquid chromatography (GSLC), commonly offer a wider range of selectivity of related molecular types than does gas-liquid chromatography (GLC).

Thus, any approach that reduces or eliminates the drawbacks of the use of solid adsorbents has potential value.

In packed column GLC a liquid is distributed on an inert solid support. To a reasonable degree of approximation the characteristics of the support largely determine the magnitude of the gas phase diffusional terms in the chromatographic rate equation, and the characteristics of the liquid and its mode of distribution on the solid determine the size of the mass transfer term. In conventional GSC, in contrast, the solid plays the part of both partitioning agent and support. If the adsorbent is, however, uniformly diluted with an inert solid the diffusional terms are likely to approach those characteristic of the diluent solid while the mass transfer term or terms should also be reduced below those typical of the adsorbent. Thus, such a packing, of appropriate composition, should have theoretical plate height (H)-velocity (\bar{v}) characteristics at least as favourable as those of a column of undiluted adsorbent and probably more so. Of greater immediate importance though is that retention times will be reduced in proportion to the dilution of adsorbent by the inert solid. The inert dilution technique thus offers the possibility of overcoming one significant inherent drawback of GSC and the certainty of reducing the extent of the other.

The literature, in this general field, stems from an early suggestion by Golay¹ relating to the surfacing of open tubes and developed for conventional packings by the Perkin-Elmer Corporation². With one exception³ subsequent work has had as its aim the development of methods to deposit layers of porous solid such as carbon, ferric oxide, zirconium oxide and organic pigments on the surfaces of glass beads⁴⁻⁶, of Chromosorbs⁷⁻⁹ or of polyethylene¹⁰ and, of course, the development of similar solids for high-performance liquid chromatography (HPLC). A majority of gas chromatographic (GC) papers^{4-6,9} are directed specifically at improving the solvent carrying capacity and theoretical plate heights (HETP) of glass bead GLC columns, the remainder aimed at improving the HETP of predominantly, carbon black GSC columns. The most successful work, in terms of HETP attained, appears to be that of Pope¹⁰, one of the earliest in the field, who partially melted carbon black into polyethylene and achieved column efficiencies normally over 500 theoretical plates per foot, and often over 750, a very remarkable achievement in GSC that seems to have attracted little attention subsequently.

The work most directly relevant to that presented here, which is directed at the use of solid particle mixtures rather than of films or bonded layers, is that of Bombaugh who, in a very brief communication³, showed that 200 mesh molecular sieve 5A (13% w/w) dry-mixed with 80 mesh Chromosorb gave a very significantly lower HETP for oxygen and nitrogen elution than did a 100% (pelleted) 5A column of similar retention.

The significant matter of retention time reduction has, of course, been demonstrated *inter alia* in a number of the papers referred to above. However, it does not seem to have been identified as a primary advantage but, rather, as an acceptable spin-off of, first, the lower HETP achieved and, secondly, the more favourable flow characteristics which permit higher flow-rates to be used.

RESULTS

Before proceeding to a direct analytical test of the proposal we present evidence in support of its basis. In Fig. 1, $H-\bar{u}$ curves for elution by nitrogen at 50° of isobutane from columns (670 cm × 2.6 mm I.D.) of silanized Chromosorb G. The data points for elution from both a 100–120 mesh (ASTM) and a 120–140 mesh column fall on the common line (a); the line drawn in the figure corresponds to the equation (units are cm and sec)

$$H = 0.110/\bar{u} \quad (1)$$

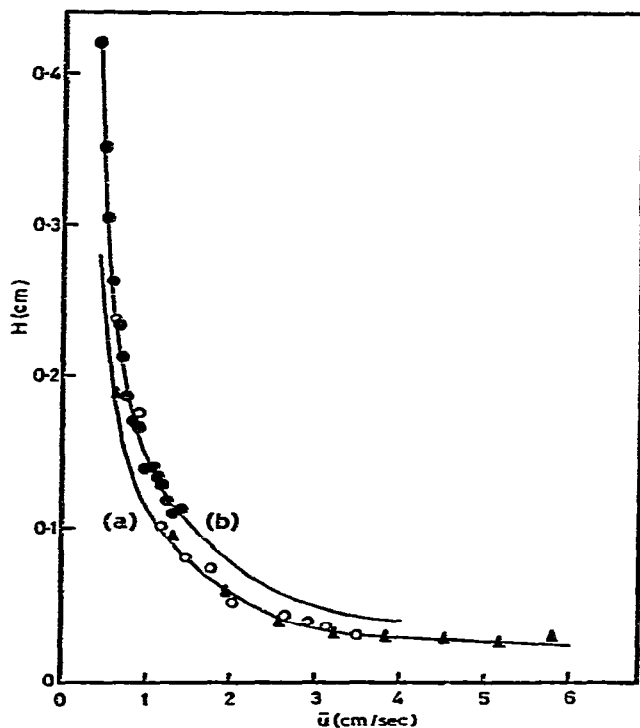


Fig. 1. Plots of H against \bar{u} for elution in nitrogen at 50° of (a) isobutane from Chromosorb G AW DCMS: open circles, 120–140 mesh (ASTM); triangles, 100–120 mesh and (b) ethane from Chromosorb P (100–120 mesh). Column (a), 670 cm × 2.6 mm I.D.; column (b), 366 cm × 2.6 mm I.D.

The second curve shown, (b), comprising data for ethane elution from an identical column of 100–120 mesh silanized Chromosorb P, is well described by

$$H = 0.155/\bar{u} \quad (2)$$

Hence, both columns act essentially as non-sorbing diffusers. This view is borne out by the fact that the ratio of the numerical terms of eqns. 2 and 1 is 1.409, while the

theoretical value of the ratio of the nitrogen interdiffusion coefficients of ethane and isobutane, according to Hirschfelder *et al.*¹², is 1.484. These two solids can be regarded, therefore, as suitable inert diluents, at least for alkane analyses.

Fig. 2 illustrates the correctness of the second assumption. The three curves show $H-\bar{u}$ plots for ethane elution from 366 cm \times 2.6 mm I.D. columns of, respectively, (a) Chromosorb G, (b) a 10:1 (w/w) mixture of Chromosorb G- Al_2O_3 (Alcoa F-20) and (c) from a 92 cm \times 2.6 mm I.D. column of Al_2O_3 . The use of a shorter Al_2O_3 column was dictated by the need to achieve velocities of reasonably high value which would necessitate unattainable high inlet pressures for longer columns of such high retention. Due to the narrowness of the very rapidly eluted bands we were unable to obtain worthwhile values of H at $\bar{u} > 4$ cm/sec for the other columns. Thus, the relevant curves are incomplete. However, the pattern is clear. As anticipated, the diluted column has characteristics at low \bar{u} , where the B term dominates the rate equation, close to those of the diluent, but at high \bar{u} , where mass transfer dominates, it shows behaviour more closely approaching that of the Al_2O_3 columns. Clearly, there is close to a two-fold gain in column efficiency at the optimum velocity (*ca.* 2.3 cm/sec) on diluting the Al_2O_3 . As expected, of course, retention times were much reduced on going from columns (c) \rightarrow (a), there being near identical (*i.e.* essentially zero) retention of C_1 - C_4 alkanes with column (a).

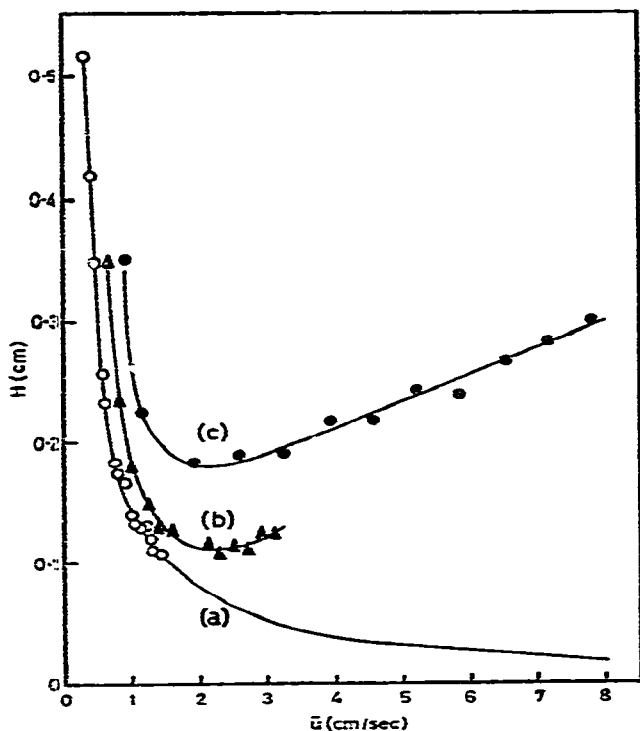


Fig. 2. Plots of H against \bar{u} for elution of ethane in nitrogen at 50° from (a) 366 cm \times 2.6 mm I.D. column of Chromosorb P; (b) 366 cm \times 2.6 mm I.D. column of 10:1 (w/w) Chromosorb P- Al_2O_3 (Alcoa F-20); (c) 92 cm \times 2.6 mm I.D. column of Al_2O_3 .

Fig. 3 illustrates a comparison of $H-\bar{u}$ curves for elution of propane by nitrogen at 50° from $366 \text{ cm} \times 2.6 \text{ mm}$ I.D. columns packed with 10% mixtures of Al_2O_3 with (a) 120–140 mesh Chromosorb G and (b) 100–120 mesh silanized glass beads. The curves on the low velocity side are coincident, as is the minimum. However, on the high velocity side, the glass bead mixture is very clearly superior due, no doubt, to the absence of porosity, the greater uniformity of shape and the somewhat reduced surface area. It would have been expected that the glass beads would represent the better diluent in view of earlier work^{4,6-9}.

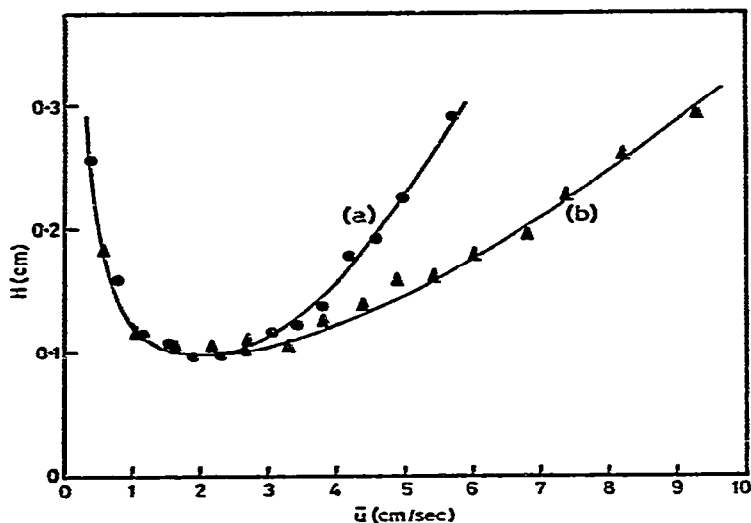


Fig. 3. Plots of H against \bar{u} for elution of propane by nitrogen at 50° from (a) 120–140 mesh Chromosorb G AW DCMS + 10% (w/w) Al_2O_3 and (b) 100–120 mesh glass beads + 10% (w/w) Al_2O_3 .

Fig. 4 illustrates the variation of fully corrected retention volume per gram of packing with % (w/w) composition of silanized Chromosorb G– Al_2O_3 mixtures for elution of (a) propane, (b) acetylene, (c) allene and (d) n -butane. We represent the data as retention per unit weight because the disparity in density of the two solids causes columns of identical dimensions to contain different weights of packings. The curves shown are surprising in that they are clearly non-linear. Further, the non-linearity corresponds to a very considerably reduced retention per gram at low Al_2O_3 contents, the more or less linear region, 0–10%, extrapolating to about one-half the observed value at 50% for each curve, while the value at 50%, in turn, is less than half that determined with undiluted Al_2O_3 . We have made repeated measurements to confirm this curvature and are forced to accept its reality. Further confirmation comes from the fact that relative retentions over the whole range have the essentially constant values: n -butane, 1.00; allene, 0.763 ± 0.0433 ; acetylene, 0.466 ± 0.060 ; propane, 0.267 ± 0.025 . There is no very evident explanation of this behaviour, particularly since, when Al_2O_3 is mixed with glass beads, the corresponding plots are certainly linear to 50%. Plot (e) of Fig. 4 shows the data for n -butane elution, for example; we do not include the data for the other three compounds for clarity of presentation. However, as is shown later, beyond 50% there is some curvature in the data for at

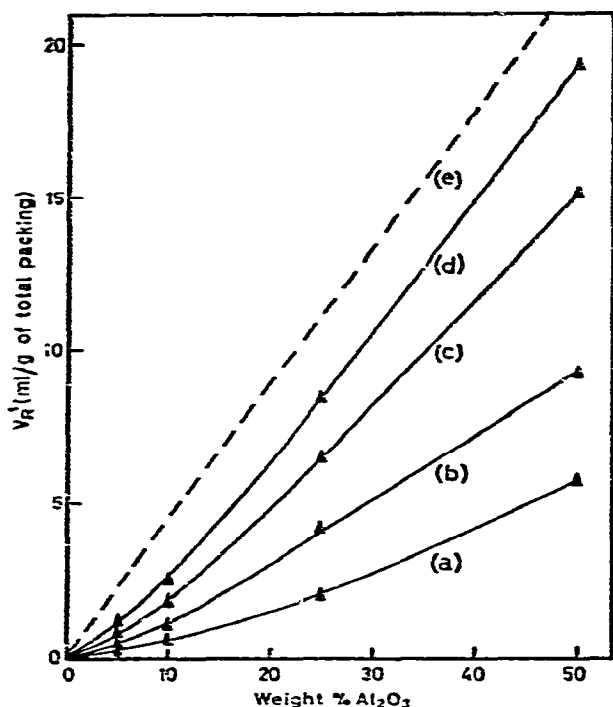


Fig. 4. Fully corrected retention volume per gram of mixed packing as a function of % (w/w) Al_2O_3 mixed with Chromosorb G AW DCMS. (a) Propane, (b) acetylene, (c) allene, (d) *n*-butane, (e) *n*-butane eluted from Al_2O_3 -glass bead mixtures.

least some substances. The curvature of these plots can be superficially ascribed to adsorptive anisotropy of the alumina particles, a feature of the dilution approach is that much smaller particle sizes than are usual are used. The discrepancy between the data for glass bead and Chromosorb columns may then be related to their relative hardness which would influence the extent of break-up of the alumina on mixing.

Fig. 5 shows some illustrative chromatograms of representative C_1 - C_4 aliphatic hydrocarbon mixtures. Elutions were by nitrogen at 50° from $366 \text{ mm} \times 2.6 \text{ mm}$ I.D. columns operated at $24 \pm 1 \text{ ml/min}$ outlet flow-rate. Fig. 5a shows the result obtained with a 10% (w/w) Al_2O_3 -glass bead column, Fig. 5b that with a 14% (w/w) column and Fig. 5c that with 100% Al_2O_3 . Inlet pressures were all in the vicinity of 60 p.s.i. and so, variation of the compressibility factor, j , was not very significant. Taking the methane elution time as the dead time we find that for (a) and (b) the relative retentions are, to within experimental accuracy, in proportion to the % Al_2O_3 . The same is true of the C_1 - C_3 group in (c) also, but both the allene and *n*-butane are more strongly retained at 100% than would be proportionate. This feature was to be expected in the light of the discussion of Fig. 4. It also establishes an interesting further feature of the dilution technique; it is self-evident from Fig. 5 that the separation of allene and *n*-butane is better with the diluted than with the pure Al_2O_3 column. We thus see that an extra selectivity factor, which can be turned to advantage,

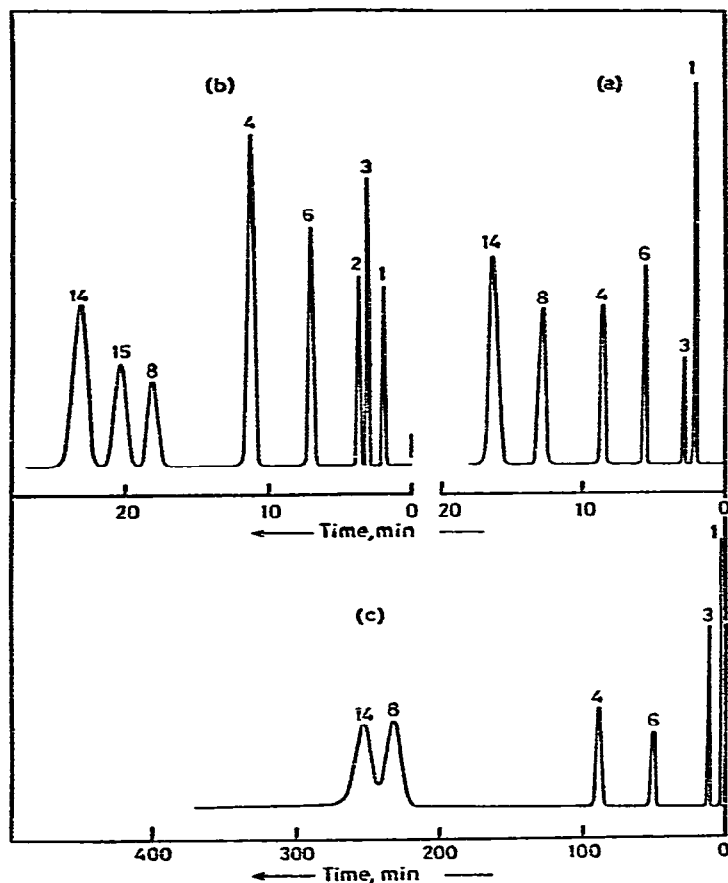


Fig. 5. Chromatograms of representative C_1 - C_4 aliphatic hydrocarbon mixtures eluted from $366 \text{ cm} \times 2.6 \text{ mm}$ I.D. columns by nitrogen at 50° . (a) 10% (w/w) Al_2O_3 -90% glass beads; (b) 14% (w/w) Al_2O_3 -86% glass beads; (c) 100% Al_2O_3 . Refer to Fig. 6 for identity of sample components.

is introduced by inert dilution. This is, presumably to be associated with the effect noted earlier wherein retentions were not linearly reduced with dilution.

Finally, in confirmation of the type of results illustrated in Figs. 1-3 it is worth noting that columns (a) and (b) are dramatically more efficient than is (c). For allene, for instance, columns (a) and (b) yield 3250 ± 150 theoretical plates ($H \approx 0.1 \text{ cm}$) whereas, with column (c) the allene peak yields only 1900 theoretical plates ($H \approx 0.2 \text{ cm}$). There is thus no question but that the original hypothesis is proved correct both in terms of improvement in efficiency and of time of analysis.

Fig. 6 illustrates chromatograms of mixtures of sixteen of the stable C_1 - C_4 aliphatic hydrocarbons. Both experiments involved elution from $762 \text{ cm} \times 2.6 \text{ mm}$ I.D. columns by nitrogen at 25° . Fig. 6a illustrates the use of a packing of 4.75% (w/w) of Al_2O_3 mixed with 100-120 mesh Chromosorb G AW DCMS while Fig. 6b shows the results for a column of 9.5% (w/w) Al_2O_3 . The flow-rates were not optimised in either case, nor were they equalised; flow-rates were, for convenience in presentation, simply adjusted to elute methane in exactly the same time. It is worth noting

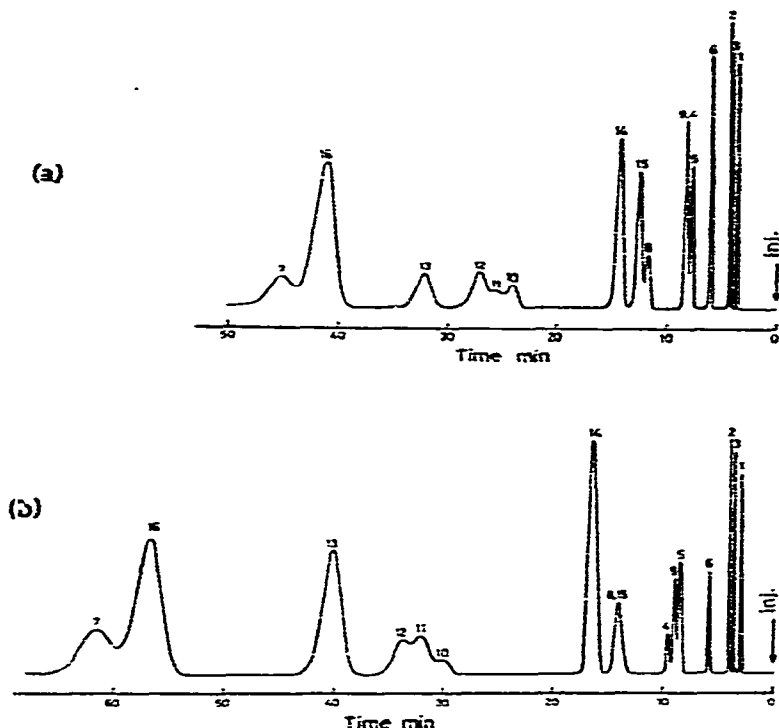


Fig. 6. Chromatograms of 16 component C_1 - C_4 aliphatic hydrocarbon mixture eluted from 762 cm \times 2.6 mm I.D. columns by nitrogen at 25°. (a) 4.75% (w/w) Al_2O_3 in Chromosorb G; (b) 9.50% (w/w) Al_2O_3 in Chromosorb G. Peaks: 1 = methane, 2 = ethene, 3 = ethane, 4 = ethyne, 5 = propene, 6 = propane, 7 = propyne, 8 = allene, 9 = cyclopropane, 10 = but-1-ene, 11 = isobutene, 12 = *trans*-but-2-ene, 13 = *cis*-but-2-ene, 14 = *n*-butane, 15 = isobutane, 16 = buta-1,3-diene.

that these columns would both, in the same conditions, separate cyclobutane and the butynes as well. With the exception of two overlaps, therefore, they would adequately resolve all stable C_1 - C_4 aliphatics in a single run. Columns of twice the length would achieve total resolution at the 2σ level. These chromatograms again show that selectivity is to some extent affected by the % Al_2O_3 present, an effect exacerbated by the use of Chromosorb G, rather than glass beads (*cf.* Fig. 4). While we showed earlier that, for the test adsorbates, the relative retentions were reasonably independent of % Al_2O_3 even though the V_g -% Al_2O_3 plots were curved, the variations for peaks 4, 9, 8 and 15, evident in Fig. 6, means that for some of the C_1 - C_4 aliphatics this is not true. This observation adds further interest to the problem uncovered here.

Finally, we show examples of the way in which inert dilution can be used to enhance the effect of turning from GSC to GLC. In an earlier paper¹¹ we have shown how Al_2O_3 -involatile liquid mixtures can be used to achieve complete separation of all stable C_1 - C_4 aliphatics in a single isothermal run. The separations there illustrated¹¹ required total analysis times of around 20% of those required to achieve total separation with columns of uncontaminated Al_2O_3 . Even so, analysis times were long, in the region of 3 h or more. Fig. 7 shows chromatograms of seventeen component

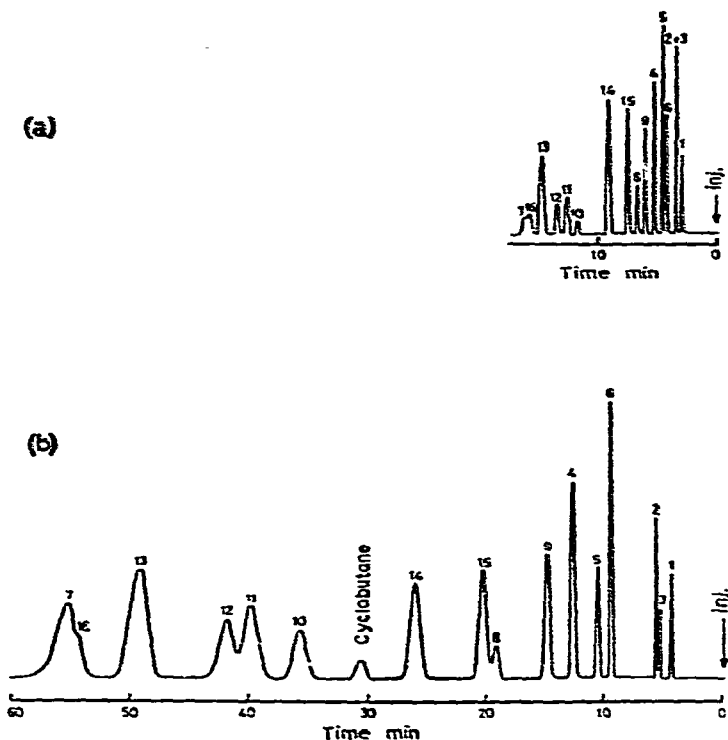


Fig. 7. Chromatograms of 17 component C_1 - C_4 aliphatic hydrocarbon mixture eluted by nitrogen from a 366 cm \times 2.6 mm I.D. column of 10% (w/w) (Al_2O_3 , 92.75%-squalane 7.25%) with 90% Chromosorb P. Elution in nitrogen (a) 40°, (b) 25°.

mixtures of C_1 - C_4 aliphatics obtained with a 366 cm \times 2.6 mm I.D. column of 10% (w/w) of Al_2O_3 (carrying 7.25%, w/w, of squalane) with 90% of Chromosorb P. Chromatogram (a) corresponds to elution in nitrogen at 40°, the run being conducted far from the optimum velocity in order to achieve a very rapid result. With the exception of two pairs there is complete separation in sixteen minutes, a very considerable achievement. Chromatogram (b) shows the result obtained at 25°, near to optimum velocity. Here, only peaks 7 and 16 overlap and a column of about 40% extra length would undoubtedly provide full 2σ resolution of this pair. Since this column will also resolve the butynes we have a system capable of separating all stable C_1 - C_4 in a time of between 1 and 2 h, a very acceptable situation.

DISCUSSION

The results of this study provide further confirmation of the view that the utility of GSC (and of GSLC) may be very considerably extended by the inert dilution technique. Column efficiencies comparable with those of GLC may be routinely achieved without recourse to special coating techniques, while very substantial reductions in analysis times may be gained. The latter may, as desired, be traded off for reduced temperatures, as is well illustrated in Figs. 6 and 7, which are effectively

room temperature analyses involving mixtures of boiling range in excess of 200°. The option of low temperature analysis opens up possibilities of analysing a wider range of sample types than has been usual in GSC.

Finally, as briefly mentioned earlier, the method seems likely to have value in HPLC when reduction of retention without sacrifice of the intrinsically high column efficiency is desirable.

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