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Note

Dusted columns: an approach to enhancement of gas–solid chromatography

W. K. AL-THAMIR and J. H. PURNELL

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

and

R. J. LAUB

Department of Chemistry, Ohio State University, Columbus, Ohio (U.S.A.)

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We have recently presented[1] evidence establishing the merits of gas–solid chromatographic (GSC) packings comprising mixtures of active and inert solids. We have shown that, with respect to GSC, much improved height equivalent to a theoretical plate (HETP) is attainable and that analysis times can be reduced very greatly without loss of resolution. The latter feature provides the alternative option of operation at much lower temperatures than are usual in GSC. These observations have led us to consider the possibilities of "dusted" columns, *i.e.* columns containing packings comprising an "inert" support dry-mixed with a very small amount of active solid since such columns would retain the advantages of inert dilution and extend the boiling range of analysable samples even more due to the further reduced retention.

Surface coated "inert" support solids have, of course, attracted a certain amount of attention in the past[2–8]. However, the main aim has apparently been to provide a uniform support of greater surface area than is provided by hard core gas–liquid chromatographic (GLC) supports such as glass, metal, or plastic beads[3–6,8]. In only one of these studies was the GSC application checked and the chromatograms illustrated indicate very poor HETP. In two instances[2,7], the intent was to provide an improved carbon-black GSC system. Excellent HETPs were achieved, particularly by Pope[2], and some interesting chromatograms were illustrated. However, the isotropy and essentially non-polar nature of carbon black is a limiting feature of this application.

A common feature of all earlier studies[2–8] has been the conscious attempt to produce tightly bonded layers; in essence, films. This aspect is particularly emphasised in several studies[3,4]; according to one group, this demands that the active solid deposited exists in particulate form of less than 1-μm diameter and that special techniques of deposition are required. This would appear to be the common view since, in all the work referred to[2–8], the deposition technique is highlighted. We know, however, and accepted open-tube technology, as well as household experience, confirms this, that finely divided active adsorbent particles adhere readily to most common materials. Further, we must ask whether in a column wherein the inert

solid effectively defines the column efficiency[1], adhesion of the active solid is particularly important. We take the view that emphasis on deposition technique in the past has not only contributed to the relative lack of interest in such packings but has also obscured the considerable potential of highly diluted GSC packings prepared by simple mixing. We present here a volume of evidence in support of this proposition which relates to what we have chosen to call dusted columns.

RESULTS

Dusted colum packings were prepared simply by mechanically mixing up to 5% (w/w) of Al_2O_3 (Alcoa F.20) with 100–120 or smaller mesh inert solid. The mixture was then re-sieved. No attempt was made to determine the amount of residual Al_2O_3 but the chromatographic retention data generally indicated amounts in the range 1–4% (w/w). Elution was in all instances by nitrogen.

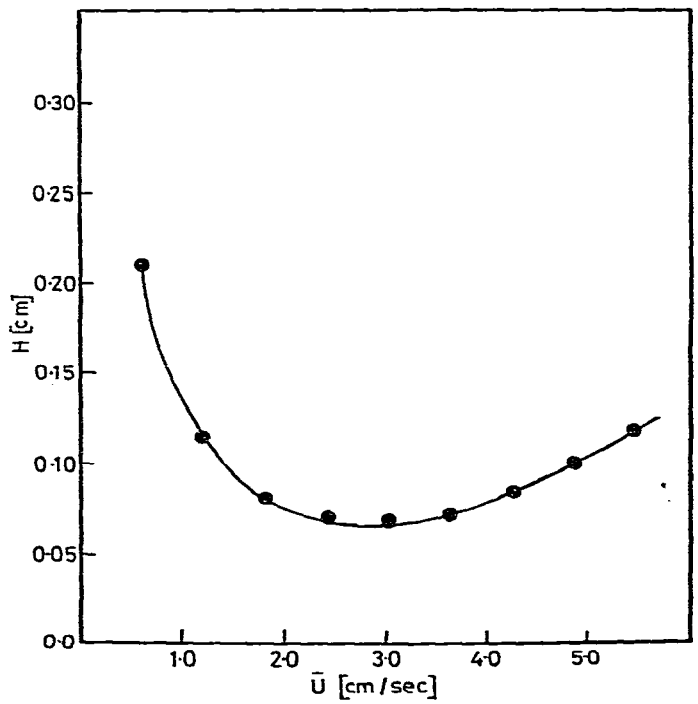

Fig. 1. H *vs.* $\bar{u}$ plot for elution of *n*-butane ($k' = 2.6$) from a dusted column of 140–170 mesh Chromosorb G with untreated Al_2O_3 (Alcoa F. 20). Carrier gas, nitrogen: elution at 50°.

Fig. 1 illustrates the very high efficiencies attainable with a dusted column. The minimum HETP attainable for *n*-butane at 50° with an Al_2O_3 dusted, 140–170 mesh Chromosorb G AW DCMS packing is seen to be around 0.065 cm (*ca.* 500 theoretical plates per foot). This is, by GSC standards, an exceptionally good value and the value would be somewhat smaller still for a component of higher k'. So far as we are aware, only Pope[2] has done as well or better with a GSC system.

Fig. 2 shows a series of 50° chromatograms obtained with 670 cm × 2.6 mm

I.D. dusted columns conta ing Al_2O_3 previously washed, and then dried under vacuum, with (a) acetone, (b) thiophene and (c) *n*-hexane. The inert diluent in (a) and (c) was 100–120 mesh glass beads whilst in (b) it was 100–120 mesh Chromosorb G. Flow-rates were neither optimised nor equalised but adjusted to allow elution of methane at constant times. The sample components are listed by number in Table I, the differences in relative retention (*e.g.* groups 8, 14, 15 and 4, 5, 9) stem from the pre-treatment with volatile liquid, a procedure having dramatic effect on the adsorptive characteristics of the Al_2O_3, as we have previously described in detail[9]. Although, in no case was flow-rate optimised, HETPs are all less than 0.11 cm (*ca.* 300 theoretical plates per foot), a value that would be entirely acceptable in many GLC analyses.

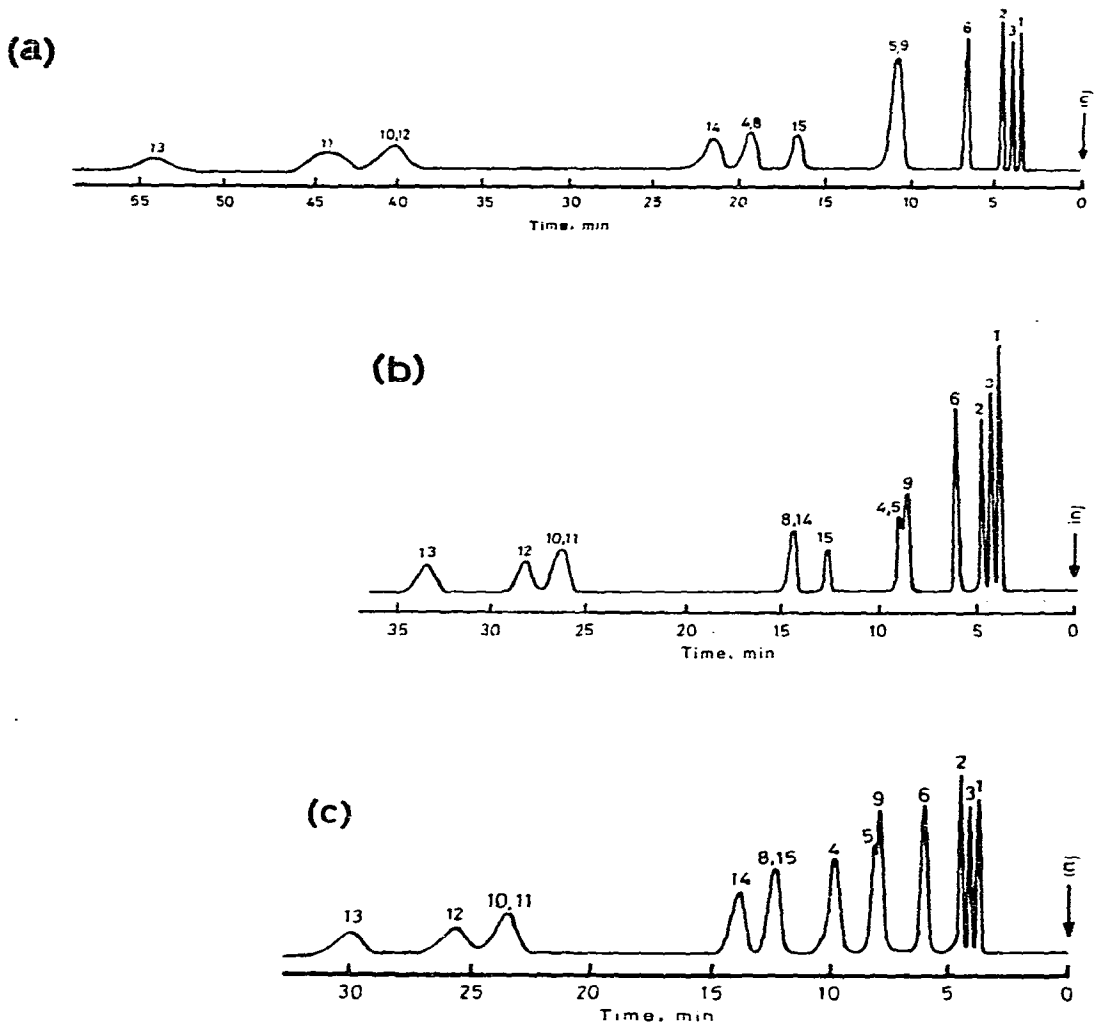

Fig. 2. Elution by nitrogen at 50° of fourteen component mixture of C_1–C_4 aliphatic hydrocarbons from columns containing Al_2O_3 pre-treated and then vacuum desorbed by (a) acetone, (b) thiophene, (c) *n*-hexane. Inert diluent: (a) and (c), 100–120 mesh glass beads; (b) 100–120 mesh Chromosorb G (AW DCMS). Key to sample components in Table I.

TABLE I

KEY TO SAMPLE COMPONENTS IN CHROMATOGRAMS OF FIGS. 2 AND 3

Peak No.	*Compound*	*Peak No.*	*Compound*
1	Methane	9	Cyclopropane
2	Ethene	10	But-1-ene
3	Ethane	11	Isobutene
4	Acetylene	12	*trans*-But-2-ene
5	Propene	13	*cis*-But-2-ene
6	Propane	14	*n*-Butane
7	Propyne	15	Isobutane
8	Allene	16	Buta-1,3-diene

Finally, we show in Fig. 3 a chromatogram of a sixteen component C_1–C_4 aliphatic hydrocarbon mixture. This was obtained with a 1524 cm × 2.6 mm I.D. column containing untreated Al_2O_3 on 140–170 mesh Chromosorb G. The efficiency, in this example, is around 400 theoretical plates per foot length of column. This is a particularly impressive chromatogram since there are very few examples of the total separation of this mixture in reasonable time[1,9]. Indeed, with appropriate modification of conditions[9] an even shorter analysis time could have been achieved.

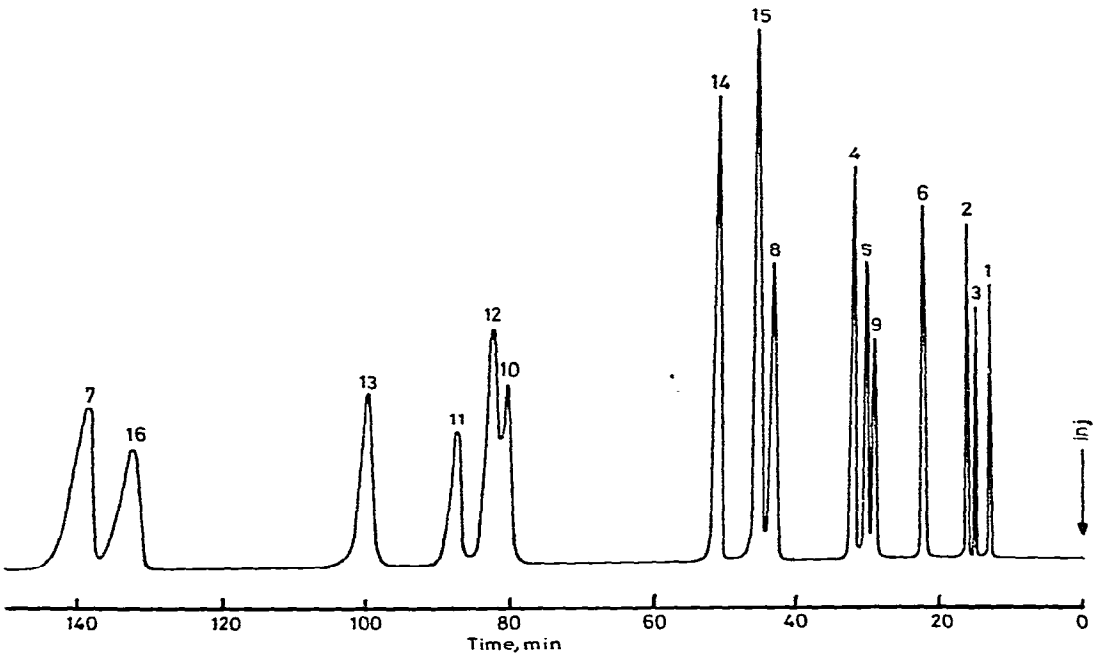

Fig. 3. Elution by nitrogen at 50° of sixteen component C_1–C_4 aliphatic hydrocarbon mixture from 1524 cm × 2.6 mm I.D. column of Al_2O_3 dusted on 140–170 mesh Chromosorb G (AW DCMS). Key to sample components in Table I.

DISCUSSION

The examples presented establish clearly that dusted columns provide highly efficient columns which permit rapid, isothermal elution of wide boiling range

samples. The simplicity of their construction and the ease with which the current results have been obtained emphasise the technical attraction such columns offer. There is, obviously, much yet to be learned regarding their mode of operation but the provisional evidence is that, (a) HETP is determined by the diluent while, (b) retention is determined by the adsorbent. The indications are thus that the two column components act independently.

We have made excellent dusted columns using, among other things, both insoluble starch and anhydrous sodium sulphate as diluents. The latter is not inert and its effect on retention was clearly discernible. Its surface cannot, therefore, be significantly excluded by filmed coverage. It seems probable, therefore, that the alumina may be present both as an adhering film and as discrete particles. Whatever may eventually emerge, regarding the physical constitution of dusted columns, they seem clearly to offer a useful approach which should find its widest application where high boiling materials or wide-boiling mixtures are to be analysed. In this context one may draw the parallel with coated open-tube columns which offer precisely the same advantages as dusted columns, but much greater technical problems of construction and handling.

Finally, and we are much indebted to Dr. C. S. G. Phillips for pointing this out, dusted columns offer a new and advantageous approach to studies of on-column catalysis since the characteristics outlined here indicate that dusted columns are free of most of the difficulties associated with columns of undiluted catalyst in catalytic work.

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