HIGH EFFICIENCY GLASS BEAD COLUMNS FOR GAS CHROMATOGRAPHY

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INTRODUCTION

For a number of years, glass beads have been used as a solid support for gas chromatography. Their main advantage lies in the greater speed of separation compared with that obtainable from a conventional column. However, glass bead packings show a poor fractionating efficiency compared with other types. In this laboratory

(b) Nickel and gold deposits were produced on the surface but no improvement over untreated beads was found. In fact, the metal-coated beads usually displayed greater adsorption than the glass ones.

3. Particulate coatings

Particles of diameter 10 μ or less will adhere quite strongly to the surface of the beads in the presence of the liquid stationary phase because of the surface tension of the liquid. It was argued that the addition of particles to the surface of the beads should produce the required roughness to give efficient spreading of the liquid. The types of particle tried fall into two main classes—spherical and irregularly shaped.

(*a*) *Spherically shaped.* Two types were tried, *viz.* micro glass beads and titanium dioxide. Micro glass beads of about 1 μ diameter were added in 1 % w/w quantity to the larger beads together with 0.5 % w/w squalane. Titanium dioxide also, with spherical particles of 0.25 μ diameter (Du Pont pyrolytic product) was tried. Quantities used were 1.5 % w/w titanium dioxide, 0.5 % squalane.

In both the above cases no improvement in efficiency over untreated beads was found. This is probably due to the same effect as with untreated beads: the liquid resides mainly at the points of contact, thus giving a very non-uniform layer of liquid.

(*b*) *Irregularly shaped particles.* A variety of powders was tried in this category, including inorganic salts, titanium dioxide and diatomaceous earth.

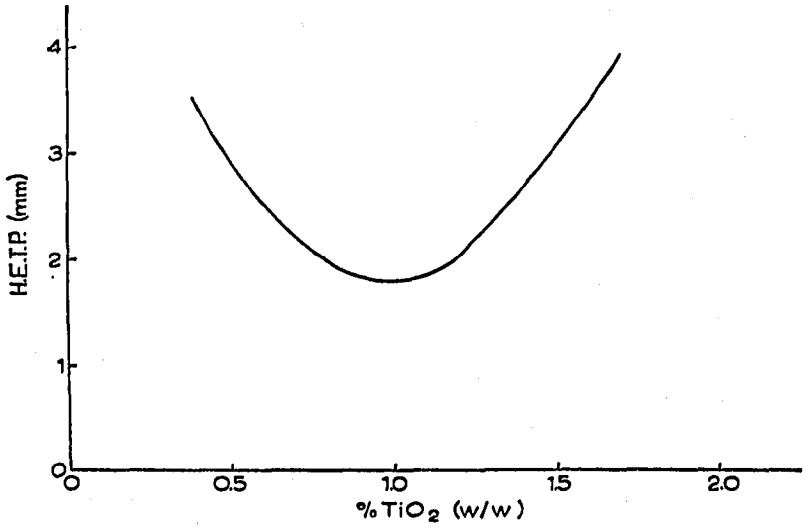

Fig. 1. Effect of additions of ordinary pigment grade titanium dioxide (0.25 % squalane).

The inorganic salts ($BaSO_4$, $BaCO_3$, $CaCO_3$) were prepared in finely divided form and added to the beads in 1.5 % w/w quantity together with 0.5 % w/w squalane. In all cases an improvement in efficiency was noted (HETP = 2.0 mm), however, the peaks tailed badly. This tailing was attributed to the polar nature of the salts.

Various amounts of titanium dioxide of irregular particle shape (conventional rutile pigment grade) were added to the beads containing 0.25 % w/w squalane. The efficiencies obtained show a maximum when plotted against weight of titanium dioxide added (Fig. 1). The best efficiency obtained was HETP = 1.7 mm.

"Celite" 501 and 541 were mixed in 1.5 % quantities with glass beads containing 0.5 % squalane. The efficiencies obtained were HETP = 1.7 mm.

The best results were obtainable with a very fine diatomaceous earth (Johns–Manville "Super-Floss").

The effect of varying both liquid and solid loading on the beads was studied using "Super-Floss" and the results are shown in Fig. 2.

The best efficiency obtained was at a loading of 0.25 % w/w squalane and 1.25 % w/w "Super-Floss" giving HETP = 0.8 mm.

For a given liquid loading the maximum efficiency was found when the ratio of squalane to "Super-Floss" was 1:5.

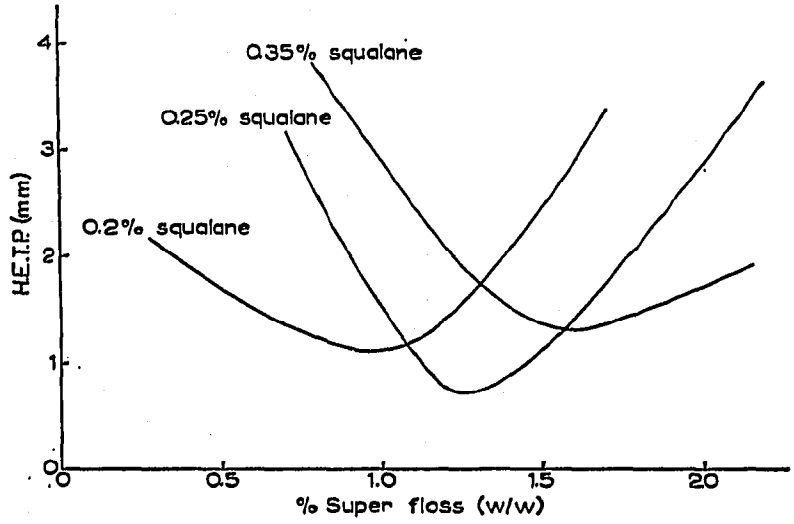

Fig. 2. Effect of "Super-Floss" at three loadings of squalane.

The preparation of the above packing is as follows:

Glass beads (60–80 mesh) are weighed out into an Erlenmeyer flask and the weighed quantity of stationary phase added. The flask is shaken vigorously to spread the liquid. If the stationary phase is too viscous, the minimum quantity of a volatile solvent required to give a solution of usable viscosity is added. The weighed amount of "Super-Floss" is then added to the beads. The mixture is shaken gently with a rotating motion for 5 to 10 min, and any lumps of "Super-Floss" are broken up with a spatula. A few small lumps of "Super-Floss" will remain. These are best left in the packing since any attempt to separate them by means of sieving will damage the particle coating. The beads are then packed into the column in the usual fashion with vibration and dumping to minimum volume.

"Super-Floss" although very fine, retains the typical diatom structures. Grinding coarser grades to similar fineness does not give an equivalent material, the diatom structure being broken down. In mixing "Super-Floss" with the beads, excessive shaking is to be avoided because of the risk of breaking down the particles.

REDUCTION OF ADSORPTION OF SOLID SUPPORT

As a result of the low liquid loading on the support, adsorption of polar compounds on the solid surfaces remains a major problem. There are two methods of at least partially overcoming this.

1. Use of a polar stationary phase

If a sufficiently polar stationary phase is used, adsorption on the solid surfaces will be suppressed. In many cases, however, a polar stationary phase may be undesirable or in fact, no suitable polar phase may be found for the desired separation. In this case a method of deactivating the polar sites on the solid surfaces by means other than the stationary phase is required.

2. Treatment with hexamethyldisilazine (H.M.D.Si.)

A method of deactivation of polar surfaces using this compound has been described[2]. However, this method was found to be long and tedious.

Effective treatment can be obtained by injection of several 2 μl lots of H.M.D.Si. into the column operating at about 120°. As the H.M.D.Si. passes through the column it reacts with the adsorptive sites on the solid support, and most of the adsorptive effects are removed.

This method has several advantages over the published method:

(a) Much simpler operation, *i.e.* deactivation is carried out while the column is in place in the chromatograph, rather than by refluxing column material for several hours, subsequent removal of solvent, etc.

(b) Less time is required. Treatment and subsequent column stabilization requires about 1 h, while other methods take more than a day.

(c) This treatment requires about 20 μl H.M.D.Si. as compared with 10 ml in the published method.

Fig. 3. shows a plot of efficiency *vs.* quantity of H.M.D.Si. added for cyclohexane and benzene. The stationary phase is squalane.

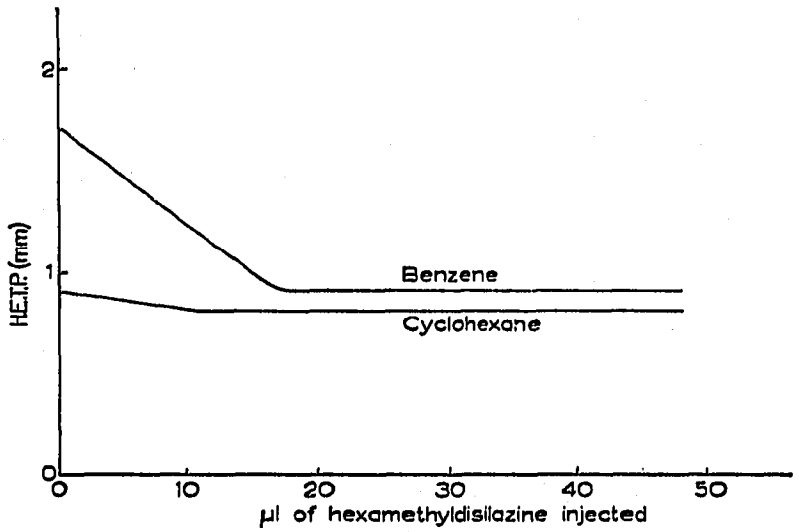

Fig. 3 Progressive effect of hexamethyldisilazine injections (squalane/"Super-Floss").

A certain amount of H.M.D.Si. remains adsorbed loosely on the support and is given off over about 1 h during normal column operation at 120°. The efficiency of the column is somewhat less for polar compounds than for non-polar compounds if a non-polar stationary phase is used. This is shown in Fig. 4, which gives a plot of

efficiency *vs.* time, beginning immediately after treatment of the column with H.M.D.Si.

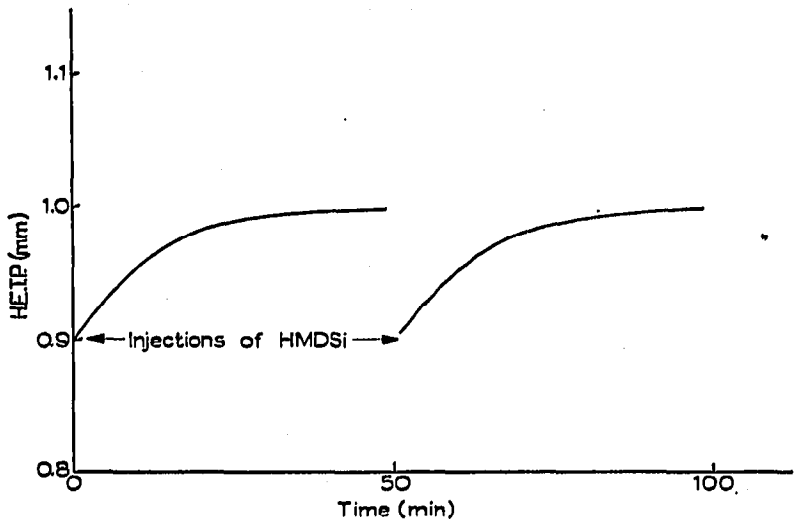

Fig. 4. Effect of loss of physically adsorbed hexamethyldisilazine (benzene on squalane/"Super-Floss").

DISCUSSION

The main source of inefficiency of glass bead columns is the non-uniformity of the depth of the stationary phase layer. This can be effectively overcome by the addition of inert particles of irregular shape onto the surface of the bead. The particles should have a diameter of about 1 to 5 μ. They are held onto the beads by the surface tension of the liquid phase, and effectively spread the liquid over the whole surface.

The maximum efficiency so far obtained reproducibly, HETP = 0.8 mm, compares very favourably with columns using solid supports such as firebrick, diatomaceous earth, etc. The highest efficiency quoted for this type of column (HETP = 0.3 mm) is better than that obtained for the modified glass beads. However, commercially available columns and most of those investigated in this laboratory give a somewhat lower efficiency, HETP = 1.0 to 2.0 mm.

The powder treatment does not, however, affect the speed of separation which makes the glass bead columns so attractive. Alternatively, a column of this type will give the same separation in similar time, but at some 100° lower than the temperature required for a conventional column. This is a considerable advantage when trace analyses are carried out at a high temperature, where bleeding of the stationary phase sets the limit of sensitivity. The effect of the treatment with H.M.D.Si is to remove adsorption caused by hydrogen bonding; it does not apparently improve adsorption effects caused by other polar forces.

SUMMARY

This paper sets out the results of an investigation into the methods of improving the efficiency of glass bead columns for gas chromatography. Efficiencies, expressed as height equivalent to a theoretical plate (HETP) of the order of 0.8 mm, as compared with 0.6 to 2.0 mm for conventional kieselguhr columns and 4.5 mm for normal glass

bead columns have been achieved. The techniques used in obtaining these efficiencies are described.

REFERENCES

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[2] J. BOHEMAN, S. H. LANGER, R. H. PERRETT AND J. H. PURNELL, *J. Chem. Soc.*, (1960) 2444.