Short Communications

Particle size nonuniformity in large scale columns

It has long been recognized that the efficiency loss of scaled up columns is a result of nonuniform column packing[1-3]. A point to point variation in solute velocity over the tube cross section leads to peak spreading and the large size prevents rapid equilibration of these variances by diffusion. An ingenious method developed by HUYTEN, VAN BEERSUM AND RIJNDERS[2] has been used to demonstrate the existence of velocity variations in a tube after it has been packed in several different ways. Unfortunately the reasons, and remedies, for packing nonuniformity have not been thoroughly understood. To aid this understanding, exploratory experiments have been made concerning the particle size distribution in a packed tube. The inferences of this study have an important bearing on the potential efficiency of large columns.

Previous work by PYPKER[4] has shown that an equal composition of 20/40 and 70/120 mesh celite will not form a homogeneous mixture in a column. The differently colored particles in each mesh category show a visual separation into layers. The present study is intended to investigate particle size variation within a narrow mesh range corresponding more to actual practice. Quantitative measurements of particle size have been made for the purpose of correlating the packing variations with previously measured[2] velocity variations.

Experimental

A pyrex column of 4.69 cm inside diameter was fixed in a vertical position. An independently supported thistle tube with its end drawn into a capillary (sufficiently small to severely restrict the flow) was centered partly within the column. A cone was formed as the particles fell into the column. After filling, a solution of hot gelatin was poured carefully into the column and allowed to percolate down through the packing material. As the gelatin seeped through air was forced out of a breathing tube at the bottom which thus prevented the formation of air pockets. An ice bath was then used to solidify the gelatin. A slight heating at the walls permitted removal of the core. Cross sections were cut midway up the tube so that end effects were of no importance. Samples were cut out at various distances from the center. The samples were washed in HNO_3, water and acetone, and then oven dried. Particles chosen at random were then measured under a microscope using a Spencer Bright-Line Hemacytometer. This device was marked off in units of 0.05 mm making readings possible to the nearest 0.01 mm. Approximately 100 measurements were made for each sample. Two measurements were made for each of the irregular chromosorb particles, one giving the maxi-

mum extension of the particle along a fixed axis and the other referring to an axis at right angles to this. This gives a better concept of the mean diameter than would be obtained by measuring the "length" or "width" of the particles.

Results were obtained with 80/100 mesh chromosorb W and 120/170 mesh glass beads. The mean particle diameter, $\bar{d}_p$, is given as a function of the distance from the tube center, r, in Table I. The standard deviation in particle size is shown with each mean value. Since the average error of measurement is probably less than 0.005 mm, this represents a true dispersion in particle size.

TABLE I

VARIATION OF MEAN PARTICLE SIZE WITH DISTANCE FROM CENTER

Column I. Chromosorb W, 80/100 mesh, light tapping
Column II. Chromosorb W, 80/100 mesh, no tapping
Column III. Glass beads, 120/170 mesh, no tapping

Column	*r (cm)*	$\bar{d}_p$ *(mm)*	*No. fines/ No. particles*
I	0.0	0.154 ± 0.027	4.96
	0.5	0.157 ± 0.032	4.10
	1.0	0.154 ± 0.033	2.86
	1.5	0.166 ± 0.030	2.80
	2.0	0.172 ± 0.036	3.18
II	0.0	0.145 ± 0.035	3.80
	0.5	0.146 ± 0.037	2.86
	1.0	0.154 ± 0.028	2.34
	1.5	0.163 ± 0.029	2.24
	2.0	0.174 ± 0.032	1.68
III	0.0	0.056 ± 0.029	
	0.5	0.061 ± 0.028	
	1.0	0.064 ± 0.024	
	1.5	0.071 ± 0.022	
	2.0	0.078 ± 0.026	

Since a large number of fines were observed under the microscope, these were counted and are reported in Table I as the number of fines divided by the number of particles. There was no problem in discriminating between fines and small particles; the former are usually no more than a tenth the size of the latter.

Discussion

Each column shows a trend from smaller to larger particle diameters as the wall is approached. For the columns which were not tapped an obvious mechanism suggests itself; the larger particles roll down the outside of the cone whereas the smaller ones are held fixed by the surface structure of the cone or penetrate into it. This mechanism

is perhaps operating to some extent with the tapped column inasmuch as some cone structure is formed and the larger particles roll more easily over the surface. This mechanism would also apply to the fines which are more numerous at the center. Some of these, however, are no doubt formed during packing and in the subsequent cutting operation. Column tapping is apparently responsible for a large number of fines in view of their increased content in the tapped column.

Irrespective of mechanism these and previous results[2,4] show that larger particles tend to accumulate at the outside and therefore greater flow velocities are expected at the outside. Attempts have been made[2] to relate the increased velocity near the outside to the wall effect of GOLAY[1], *i.e.*, the velocity increase within a half particle diameter of the wall due to a postulated increase in channel size. It is obvious, however, that the particle size variation cannot be ignored. While it is difficult to compare these two effects with the small amount of data available, a preliminary attempt is worthwhile. Since the average flow velocity of gas within a given section is roughly proportional to the square of the average particle size, the outside to inside flow velocity ratio is about 1.25 and 1.44 in the tapped and untapped chromosorb columns, respectively. This corresponds very closely to the range of velocities found by HUYTEN *et al.*[2]. Furthermore the nature of the particle size variation found here is very similar to their velocity variation, both quantities increasing rapidly upon approaching the wall. Although the two experimental systems are not comparable in an exact way, as emphasized by HUYTEN, we believe the comparison to be significant. HUYTEN *et al.* found a twelve fold increase in flow velocity necessary within a half particle diameter of the wall to explain the velocity variation for their best column on the basis of the wall effects. The required increase would be much greater for their other columns. GOLAY estimates the increase to lie between 3 and 6. The authors believe these values to be high; irregular particles are often observed to flatten themselves against a wall leaving a minimum of flow space. Most investigators, in fact, find a decreased rather than an increased velocity within a half particle diameter of the wall[5]. We may conclude, therefore, that particle size variation can easily explain the full velocity variation of HUYTEN *et al.*, but that the wall effect can only account for a small fraction, if any, of the observed variation.

It is instructive to consider the flow velocity variation which will first have a noticeable effect on column resolution. We consider here only very large columns (typically > 2 in.) which cannot be laterally traversed by solute diffusion more than once in a run. The efficiency loss will be negligible if $\sigma > \Delta v t$, *i.e.*, if the normal zone dispersion, σ, is greater than the separation caused by moving at the outside of the tube rather than the center (Δv = velocity difference, t = retention time). This condition becomes:

$$\Delta v/\bar{v} < (N)^{-1/2}$$

If $N = 1000$ plates are required, the relative velocity variation should ideally be no more than 3% and the particle size variation no more than 1.5%. While some margin can be added to this, the minimum 20% velocity variations considered here are too

large. The criterion given above should also apply to the permissible tube to tube velocity variations in a multiple tube system.

The immediate remedy to packing nonuniformity would seem to lie in more careful packing. However, it may be taken as fundamental that center and wall regions of the tube are never equivalent, and cannot be subjected to the same influences and forces. The proximity of a wall must always influence packing structure. Even in vibration, tapping and beating, different forces are operating because of energy absorption by the packing, etc. Possible solutions may be found in, (1) the trial and error discovery of packing methods which properly compensate divergent factors, (2) the use of uniform packing particles, perhaps machine made, and (3) the use of column geometries which, by symmetry or otherwise, lend themselves to uniform packing. The latter appears most promising; the annular space between two concentric cylinders has angular equivalence by symmetry and the effect of the radial nonuniformity can be obviated through control of the gap width while still maintaining very high capacities[3]. This column can also be adopted to continuous use.

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Gas chromatography of some pharmacologically active phenothiazines

While there has been widespread application of gas chromatography to the separation of naturally occurring, biologically active compounds[1-8], little work has been directed to similar compounds of synthetic origin. Since the phenothiazine derivatives are widely used in medicine, their gas chromatographic behavior is of interest to chemists, pharmacologists, and toxicologists involved in synthetic, metabolic, and analytical studies.