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GRADING OF CHROMATOGRAPHIC SUPPORTS AND PACKINGS ACCORDING TO PARTICLE SIZE BY THE FLUID METHOD

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SUMMARY

Supports and packings for chromatography were graded by the flotation of individual particles in a constant stream of gas or liquid. By gradual increase in pressure, fractions containing particles of a particular size were separated and isolated. The sharpness and the reproducibility of the separation were studied. The effect of particle shape on the sharpness of separation was investigated.

INTRODUCTION

Supports and packings, *i.e.*, sorbents and coated supports, with various particle sizes and giving various sharpnesses of selection are commercially available. The particle sizes used in gas chromatography are becoming smaller, in accordance with the work of BOHEMEN AND PURNELL[1], who described the increase in the efficiency of chromatographic columns with a decrease in size and an increase in the homogeneity of the particles of the packings. Whereas several years ago support sizes of 30–60 mesh (250–590 μm) were used, nowadays sizes of 149–177 and 125–149 μm are in general use and even supports in the range 149–163 μm have recently become available. However, all of them always contain a certain proportion of particles of smaller or larger size than the general range indicated. The composition of Chezasorb 200–400 μm

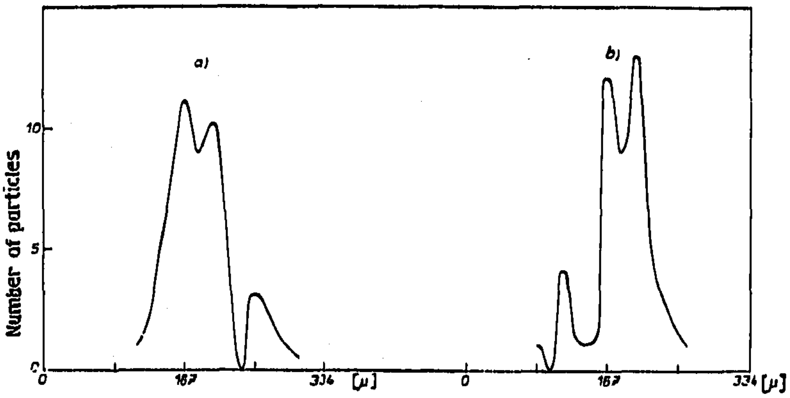

Fig. 1. Change in the distribution of particle sizes due to coating with Chezasorb: (a) before coating; (b) after coating.

(Fig. 1) is given as an example. Smaller powdery particles are obtained during sizing by mechanical sieving on sieves, and these particles become attached to larger particles. That is the reason why Purnell[2] recommended that an additional selection process should be carried out on the sieved fractions by sedimentation in water, in which those fractions that settle to the bottom of the vessel first and last are removed.

It is obvious from Fig. 1 that a certain proportion of finer particles is again obtained when coating the support by the slurry method (the solvent is evaporated from its suspension in the solution of the stationary phase). Amos and Hurrell[3] removed the powder from the coated support by blowing dry nitrogen through the column tower and trapping the powder on a cotton-wool filter. Mon *et al.*[4] used a horizontal air stream for the selection of packing fractions according to particle size and density. Smaller and lighter particles are carried further by the air stream than large and heavy ones. Cramers *et al.*[5,6] have recently shown the significance of the careful selection of the supports for microcolumn packings.

The composition of the raw materials used is checked in the ceramics industry by means of the flotation device[7] of Kopecký. The device consists of three connected vessels, the diameters of which increase gradually. The material being tested is subjected to flotation by passing a continuous stream of water through the vessels. The ascending velocity of the particles of material is lower in the wider vessels and hence particles of various sizes can be removed from the different vessels after the flotation. The particles can be graded into any required number of fractions by stream analysis[8] according to Schöne, by means of which particles of different sizes are obtained by varying the velocity of the stream.

ANALYSIS OF THE PROBLEM

For a sphere of diameter d_p, falling vertically in a liquid according to Stokes' law[9,10]:

$$F = 3\pi\eta d_p v \tag{1}$$

and according to the Hagen–Poisseuille law:

$$Q_V = \frac{\pi R^4 \Delta p'}{8\eta \Delta l} \tag{2}$$

the diameter can be expressed by the relationship:

$$d_p^2 = \frac{9R^2 \Delta p'}{4(s-\rho) g \Delta l} \tag{3}$$

where F is the resistance of the liquid to the movement of the sphere, η is the dynamic viscosity, v is the velocity of the sphere, Q_V is the total flow-rate, R is the diameter of the tube, $\Delta p'$ is the decrease in the pressure along the length, Δl, of the tube, s is the density of the sphere, ρ is the density of the medium and g is the acceleration due to gravity. The above relationships hold for Reynolds number, given by the equation

$$Re = \frac{v_m d_p \rho}{\eta} \tag{4}$$

in the range from 0.001 to 0.1. v_m is the boundary velocity at which equilibrium is established. Stokes' law holds exactly for

$$\psi Re = 3\pi \tag{5}$$

where ψ is the resistance coefficient.

For irregular particles, the diameter of the particle in the above equations is replaced by the equivalent diameter $d_{\text{equiv.}}$, which is the diameter of a hypothetical sphere of cross-section equal to that of the irregular particle. Then,

$$d_{\text{equiv.}} = \frac{8\varphi Re\eta^2}{R^2\rho} \cdot \frac{\Delta l}{\Delta p'} \tag{6}$$

where the correction coefficient φ is dependent on the particle shape and on the criterion $Re^2\psi$ (see Table I).

TABLE I

DEPENDENCE OF CORRECTION COEFFICIENT φ ON $Re^2\psi$

$Re^2\psi$	*Particle shape*				
	Globular	*Rounded*	*Angular*	*Oblong*	*Tabular*
8 000	1	0.805	0.68	0.61	0.45
10 000	1	0.80	0.678	0.595	0.441
20 000	1	0.79	0.672	0.59	0.43
50 000	1	0.755	0.65	0.564	0.42
100 000	1	0.753	0.647	0.562	0.408
200 000	1	0.74	0.635	0.560	0.392

It follows that the fluid method for the grading of supports and packings enables one to obtain supports free from the powder portion and with a grain homogeneity such that valid assumptions can be made for the preparation of column packings for high-pressure liquid chromatography that have the same particle size range as that being used in gas chromatography at present. A simple device was constructed that enabled the sharpness of the fractionation of particles, in terms of particle size and reproducibility of the separation process, to be studied.

EXPERIMENTAL

The grading was tested on the following supports and adsorbents with both regular and irregular particles: Chromosorb P, 149–177 μm; Chezasorb, 200–400 μm, coated with Vumapol; Synachrom E 5, 160–200 μm; Porasil C, 36–75 μm; glass beads, 50–100 μm; alumina, 30–300 μm; carbon molecular sieve.

The materials were studied in the apparatus shown in Fig. 2, which consists of a source of air or some other gas (A), a long, straight tube (B) which is divided in its lower section with a porous plate (C) and terminated at the top with a narrow tube to which a fraction receiver (D) is connected. A membrane pump with an output pressure of 2 atm was used as the air source, a step-down pressure regulator (E), connected to a manometer (F), was used for the regulation of air pressure and flow-rate,

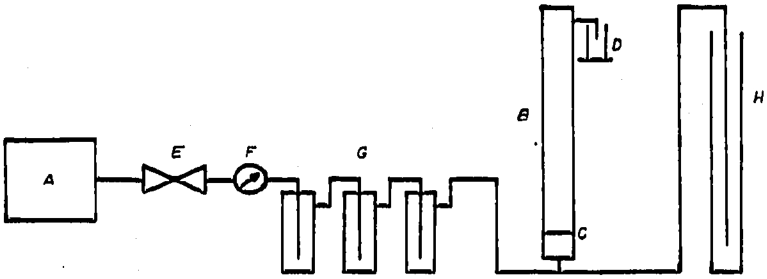

Fig. 2. Diagram of the apparatus for the grading of supports and packings.

and a system of three bubblers with porous plates as resistances (G) was used for the damping of the eventual pressure impacts. A long-lasting fine fluctuation of the pressure was balanced by a water pressure regulator (H).

A similar arrangement was used for the grading of particles with water or some other liquid. The liquid was extruded from the container by an adjusted constant over-pressure of air, and a fine adjustment of the pressure — and hence thus also the adjustment of the flow of the liquid — was made by an adjustable overflow of the liquid into a tube parallel with the grading tube. By increasing the position of the overflow, the flow-rate of the liquid was also increased.

The flow-rates of air or water were controlled by means of a pressure regulator and the readings were taken from the water manometer as the height in millimetres of the column of water (kp/m^2). Individual flow-rates were selected according to the movement of the particles being selected (*e.g.*, with Synachrom) or in intervals of 40 mm of the column of water. The device used permitted the over-pressure intervals to be set at 10 mm of the column of water.

The support or adsorbent was poured on to the porous plate in the separation tube, the fraction receiver was connected and the gas switched on. The particles were floated by the streaming gas and carried according to their size and density in such a manner that the lightest ones were transported from the tube into the fraction receiver while the others either floated in the tube or were left on the porous plate. When no more particles were moving, the flow-rate was increased and the fraction receiver changed. In this manner, the whole sample was graded into the required number of fractions.

The samples obtained by flotation were left in the fraction receiver for a certain period of time, and the liquid was later filtered and evaporated.

The evaluation of the sharpness of grading was carried out by microscopic determinations of the diameters of 20 or 50 particles. The arithmetic average and the standard deviation were calculated for this set of particles. The grading of Porasil was repeated five times and the reproducibility of the grading was calculated for all the measurements.

RESULTS AND DISCUSSION

The sharpness of the grading obtained by using the above device under the given conditions can be seen from Table II, where the results of the selection and measurements of particle diameters of Porasil C, glass beads and Synachrom E 5,

TABLE II

COMPOSITIONS OF INDIVIDUAL FRACTIONS OF PORASIL C OF PARTICLE SIZE 36–75 μm

Fraction	*Particle size* (10^{-3} *mm*)					*Average* (10^{-3} *mm*)	*Standard deviation* (10^{-3} *mm*)
I	33.4	33.4	41.8	50.1	41.8	41.8	10
	33.4	25.1	25.1	33.4	25.1		
	41.8	50.1	58.5	41.8	50.1		
	50.1	50.1	41.8	41.8	50.1		
II	50.1	58.5	50.1	66.8	58.5	52.6	7
	66.8	50.1	41.8	50.1	66.8		
	50.1	50.1	50.1	58.5	50.1		
	50.1	50.1	50.1	50.1	50.1		
III	66.8	66.8	66.8	58.5	75.1	68.7	7
	66.8	75.1	66.8	75.1	75.1		
	83.5	58.5	75.1	58.5	66.8		
	66.8	66.8	66.8	66.8	66.8		
IV	83.5	83.5	75.1	75.1	83.5	75.1	6
	66.8	75.1	66.8	83.5	75.1		
	75.1	75.1	75.1	66.8	66.8		
	75.1	83.5	75.1	66.8	75.1		
V	83.5	75.1	83.5	83.5	83.5	83.5	20
	83.5	66.8	91.8	58.5	75.1		
	91.8	58.5	66.8	66.8	125.5		
	66.8	133.6	83.5	83.5	108.6		

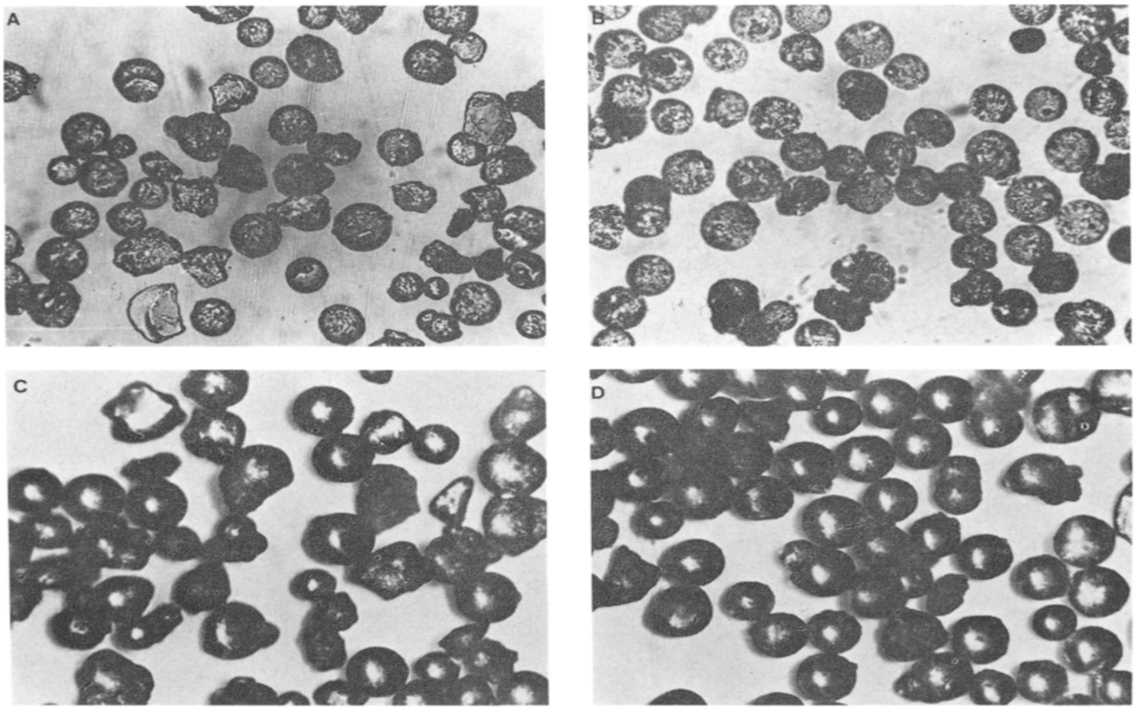

Fig. 3. (A) Non-selected Porasil C; (B) selected Porasil C (fraction III); (C) non-selected carbon molecular sieve; (D) selected carbon molecular sieve. Enlarged 100 ×.

i.e., of the particles with regular spherical shape, are summarised. The standard deviation is 6–9 μm in all instances except for the last fraction, for which the standard deviation may be even three times higher than in other fractions. This increase is caused by the non-homogeneity in the composition of the fraction, as shown in Fig. 3.

The detailed distribution of the particle diameters in the individual fractions is shown in Table III for 100 values of the diameters of Porasil particles of particle size 36–75 μm. It can be seen that the selected material also contains particles that are larger and smaller than the size range indicated on the manufacturer's packaging (see fractions I and V and Fig. 4). The compositions and particle diameters of fractions II–IV demonstrate that the fractions with a size range of 15 μm can be well separated. If the grading is limited to a size range of 7 μm, as with fractions III and IV, then particles of the same size appear in both fractions (overlapping of particle sizes in both fractions), as shown in Fig. 4.

TABLE III

GRADING OF SUPPORTS OF GLOBULAR SHAPE WITH AIR

Support	*Fraction*	*Diameter*, d_p (10^{-3} *mm*)	*Standard deviation* (10^{-3} *mm*)
Glass beads	I	52.0	6
	II	96.7	9
	III	128.6	9
Synachrom	I	167.8	6
	II	245.0	9
	III	230.5	25
Porasil C	I	43.0	10
	II	61.4	7
	III	74.0	7
	IV	86.3	6
	V	98.5	22

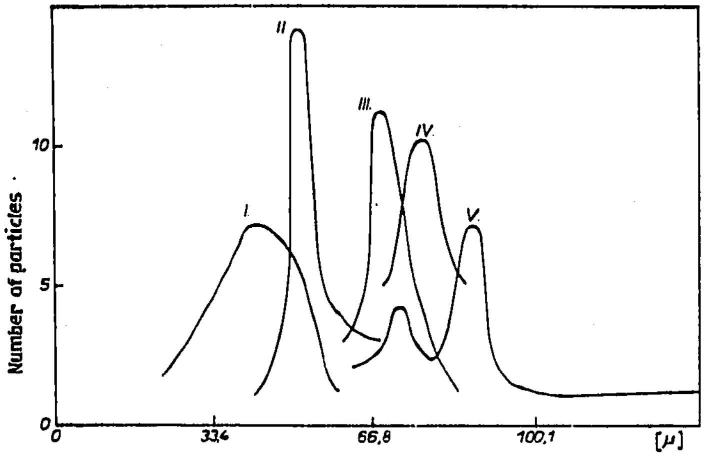

Fig. 4. Distribution of particle sizes for individual fractions of Porasil C.

Synachrom, the composition of which is shown in Fig. 5, gave two fractions, one with a particle diameter of 168 μm and the other with a particle diameter of 245 μm. The third fraction was fairly non-homogeneous and contained particles with irregular shapes; its lower diameter of 231 μm is a consequence of both of the factors. The grading of glass beads gave results that are comparable with those obtained for both of the preceding adsorbents.

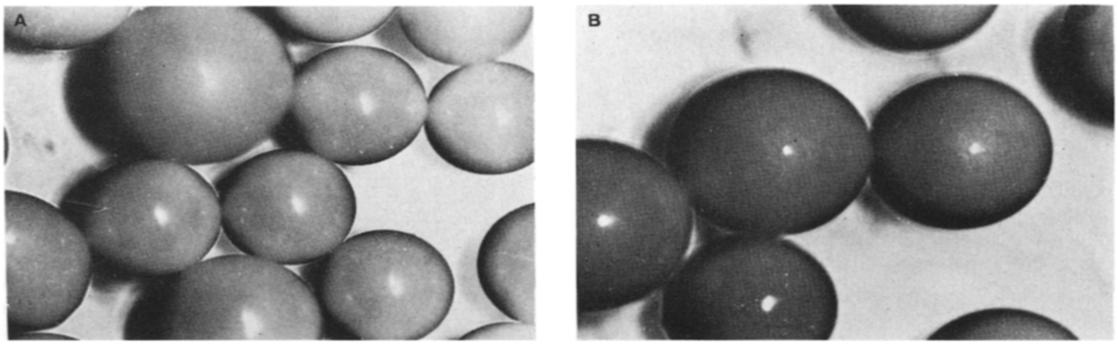

Fig. 5. (A) Non-selected Synachrom E 5; (B) selected Synachrom E 5 (fraction II). Enlarged 100 ×.

The results obtained for the graded support Chromosorb P and the coated support Chezasorb are shown in Table IV. Owing to the irregular particle shapes of both of the supports, the standard deviation is increased to 22–60 μm. The differences in density (Fig. 6) also contribute to a high standard deviation. The selected method of measurement also contributes to the increase in the standard deviation; in this method, the largest dimension of the particle is always taken as the diameter.

TABLE IV

GRADING OF PARTICLES OF IRREGULAR SHAPE WITH AIR

Type	*Fraction*	*Average particle size (10^{-3} mm)*	*Standard deviation (10^{-3} mm)*
Chezasorb	I	216.5	22
	II	273.0	10
	III	357.0	22
	IV	377.5	28
	V	392.0	45
	VI	304.0	54
Chromosorb P	I	64.8	22
	II	334.0	36
	III	384.0	22
	IV	337.2	54
	V	423.0	68
	VI	415.0	45

The reproducibility of the grading of Porasil C was also studied. The process of grading repeated five times gave the results in Table V. It can be seen that the standard deviation of individual particle diameters is about 4 μm, except for the last non-homogeneous fraction, the standard deviation of which is twice as great.

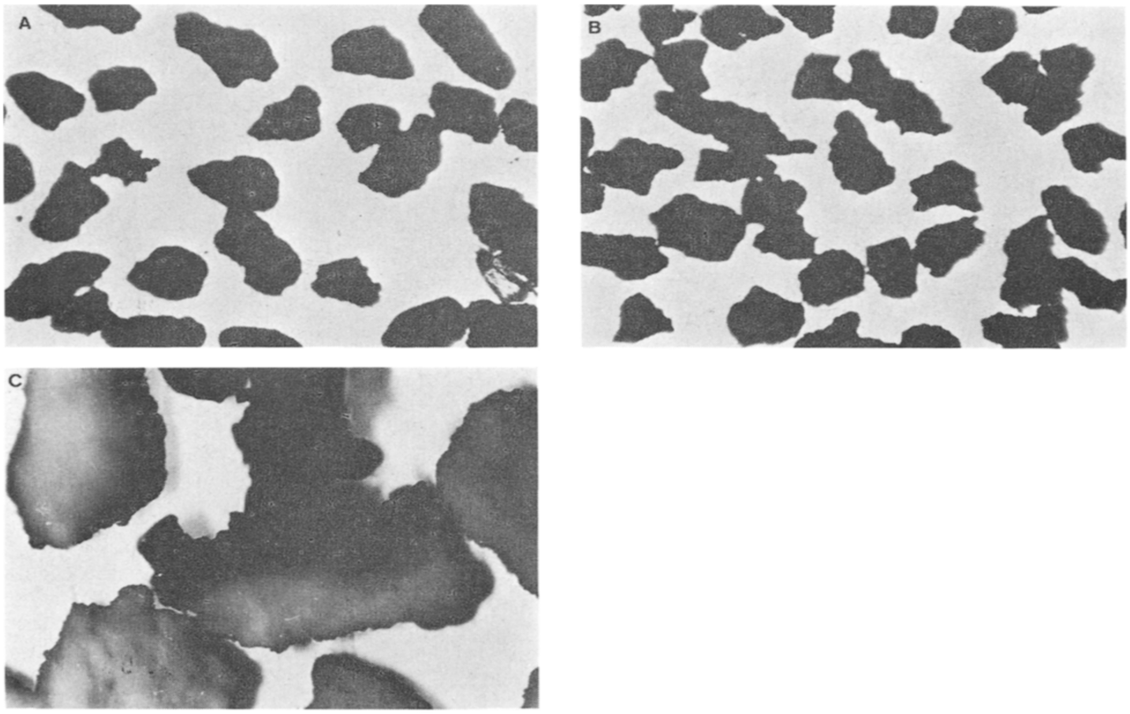

Fig. 6. (A) Non-selected Chezasorb; (B) selected Chezasorb (fraction V); (C) selected Chezasorb. Enlarged 20 × (A and B) and 100 × (C).

TABLE V

REPRODUCIBILITY OF THE GRADING OF PORASIL C

Experiment	*Fraction (10^{-3} mm)*				
	I	*II*	*III*	*IV*	*V*
1	43.0	61.4	74.0	86.3	98.5
2	46.8	58.0	70.7	79.2	91.5
3	41.8	63.5	74.7	81.0	107.4
4	41.8	52.6	68.7	75.1	83.5
5	39.3	61.4	73.4	76.8	102.2
Average ± standard deviation (10^{-3} mm)	42.5 ±2.6	59.4 ±4.3	72.3 ±2.5	79.7 ±4.3	94.6 ±9.6

The grading was repeated with water as the flotation liquid. Glass beads were again used so as to be able to compare the effects of the grading medium. The results of the measurements given in Table VI show that the flotation has an adverse effect on the grading. Also, the reproducibility of the grading was considerably worse, probably owing to imperfect regulation of the water flow-rate. The flotation with water or other liquids (methanol for Porapak flotation) is limited to the grading of supports and adsorbents; the coated supports cannot be subjected to flotation. On the other hand, liquids decrease the effect of the differences in particle densities

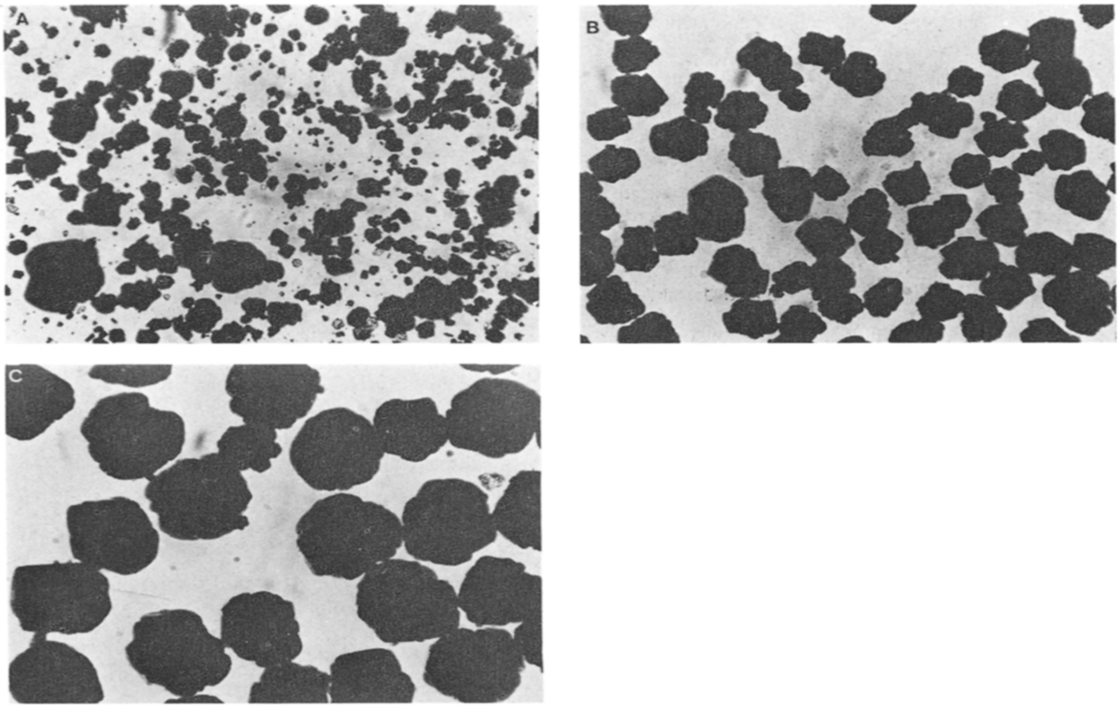

Fig. 7. (A) Non-selected alumina; (B) selected alumina (fraction III); (C) selected alumina (fraction VII). Enlarged 20 ×.

TABLE VI

GRADING OF GLASS BEADS WITH WATER AND ITS REPRODUCIBILITY

Experiment	*Fraction*	*Average particle size* (10^{-3} *mm*)	*Standard deviation* (10^{-3} *mm*)
1	I	560	22
	II	570	9
	III	802	9
	IV	964	13
	V	1308	9
2	I	566	27
	II	655	9
	III	810	13
	IV	1045	9
	V	1303	13
3	I	549	22
	II	583	9
	III	762	9
	IV	996	13
	V	1312	13

for non-homogeneous particles, and the particle diameter becomes the most decisive factor.

It follows from the relationship

$$d_p = \sqrt{\frac{18\eta}{g(s-\rho)}\cdot u} \tag{13}$$

that the particle diameter is directly proportional to the square root of the average flow-rate, u, and inversely proportional to the square root of the difference between the densities $(s - \rho)$. The deviation of the particle size with fluctuations of the flow-rate of the medium and with the non-homogeneity of particles, *i.e.*, the varying difference between the densities $(s - \rho)$, can be found from the total differential of the variables u and $(s - \rho)$:

$$\mathrm{d}(d_p) = \sqrt{\frac{18\eta}{g(s-\rho)}}\cdot\frac{\mathrm{d}u}{2\sqrt{u}} - \sqrt{\frac{18\eta u}{g}}\cdot\frac{\mathrm{d}(s-\rho)}{2\sqrt{(s-\rho)^3}} \tag{14}$$

For grading in a particular medium, the viscosity of this medium can be considered to be constant.

The standard deviation in the particle size is 2 % for the grading of particles with a regular spherical shape with a fluctuation in the flow-rate of 4 %, but for a support or the packing that contains non-homogeneous particles (*i.e.*, particles with varying densities) the particle sizes can differ by up to 50 % if the difference between the densities $(s - \rho)$ is considered to be in the range 0.8–2.1 g/cm^3 and the change in the flow-rate is also considered to be the same.

The diameter of a particle with an irregular shape

$$d_{\text{equiv.}} = \varphi\cdot\frac{Re\eta}{u\rho} \tag{15}$$

depends on the change in the correction coefficient, φ (see Table I), and the average flow-rate, u. The deviation of the particle diameters of the individual fractions is given by the total differential of the variables φ and u:

$$\mathrm{d}(d_{\text{equiv.}}) = \frac{Re\eta}{u\rho}\cdot\mathrm{d}\varphi - \varphi\cdot\frac{Re\eta}{\rho}\cdot\frac{\mathrm{d}u}{u^2} \tag{16}$$

The standard deviation of the particle diameters will increase by up to 25 % with a change in the flow-rate of 4 % and with a change in the correction coefficient within the range given in Table I. Considering that the support or the packing does not contain all the ranges of particles, the correction coefficient changes approximately within the range 0.4. The standard deviation of the particle sizes of the support or packing being graded is 12 % in this instance, which is in agreement with the results given in Table IV.

During the flotation of particles with the liquid, the density of the flotation medium influences considerably the difference in the densities $(s - \rho)$ and it therefore decreases substantially the contribution of the second term in eqn. 14 to the standard deviation of the average of the selected particles.

It follows that particles that differ in size by 1–2 µm can be separated under conditions of constant density and identical shapes of the particles. The measured values for Porasil C show standard deviations for individual fractions that are greater than those derived from the preceding considerations. They are determined by the selection of the individual air flow-rates, which were determined on the basis of practical time periods and adequate homogeneity of the particles being separated.

CONCLUSIONS

The experimental results for the grading process show that not only supports but also packings for chromatographic columns can be prepared by means of the fluid method, which are (1) perfectly free of powder-like particles of small size (Fig. 7) and (2) much more homogeneous in terms of density and particle size. Flotation with liquids permits only the grading of supports and adsorbents.

This method of grading enables packings for liquid chromatography to be prepared, the particle sizes of which differ by only 10–20 % of the diameter of individual particles (previously this difference has been up to 100% and more) and hence a facility will be created for the preparation of columns with efficiencies equivalent to those of the columns used in gas chromatography.

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