

PARTICLE SIZING BY CAPILLARY HYDRODYNAMIC CHROMATOGRAPHY

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Abstract—Liquid borne ultrafine particles have elsewhere been shown to pass through a packed column at rates varying with particle size. The process is termed “hydrodynamic chromatography”, since a separation of the particles according to size can thereby be achieved. Similar results are reported herein for larger particles suspended in liquid when the passageway, instead of being a packed column is a long, completely open, capillary tube. Particle transit time is a function of the logarithm of particle diameter. The underlying mechanism for the latter phenomena is believed to be that previously called the “tubular pinch effect” which arises from a balance of lateral forces within the flow field, but experimental results are not adequately described by any theory yet proposed. The open-tube discrimination process is designated “capillary hydrodynamic chromatography”.

INTRODUCTION

Small (1974) showed that submicrometer (colloid) particles suspended in a liquid emerged in accordance with their size, the largest first and the smallest last, when injected in a relatively small amount at the head of a column packed with styrene divinylbenzene copolymer spheres of from 18 to 58 μm in diameter and made to flow through the column by elution with more liquid. Almost complete separation of nearly monosize latices of 0.234 and 0.109 μm diameter, for example, was achieved in this manner. The liquid in which the particles were injected (identified by a marker substance) emerged after the smallest particles, i.e. all particles moved ahead of the liquid with which they were initially associated. The present explanation (Small *et al.* 1976, Ruckenstein, Marmur & Gill 1977, McHugh *et al.* 1976) for this behavior involves a combination of mechanical, electrostatic, and van der Waals force interactions. Application of the technique to latex size analysis is being increasingly applied under the terminology “hydrodynamic chromatography”.

Similar behavior—largest particles first followed in order by particles of decreasing dimensions and all particles ahead of the liquid with which they started—is shown herein also to be exhibited by micrometer-size particles when injected at the head of a long, open capillary tube and caused to pass through the tube by the flow of more liquid. Investigation of this phenomena was suggested to these authors in a private communication by Dr. D. M. Ball who discovered the existence of size discrimination in such capillary flow while testing a liquid chromatographic valving mechanism using India ink; he described the effect as “capillary hydrodynamic chromatography”. The following presents information obtained with particles flowing through capillaries and reviews the probable mechanism of the resulting size discrimination.

EXPERIMENTAL EQUIPMENT AND TECHNIQUE

The basic apparatus consisted of a liquid chromatograph pump capable of essentially constant volumetric flow output up to about 5 ml/min at pressures of about 2.8×10^4 kN/m² (Pa), a chromatographic injection valve, coiled stainless steel tubing in lengths from 88.4 to 201.2 m with internal diameters of 254 and 508 μm , an ultraviolet detector, and a strip-chart recorder. Liquid, either certified A.C.S. methanol or distilled deionized water, was passed continuously from the pump, through the injection valve, one of the stainless capillary tubes, and the u.v.

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detector. Particles for testing were first dispersed in a liquid and then injected into the system with the injection valve. Flow of liquid through the apparatus was only momentarily interrupted during the injection, the valve being designed so flow was diverted through another path while the injection portion of the valve was being loaded. Ordinarily $2\mu\text{l}$ of particle dispersion constituted the test sample. No particular particle concentration was sought as results were not noticeably influenced thereby. A 1% solution of acetone in methanol was used for particle dispersion when incorporation of a liquid marker was desired, acetone being strongly absorptive at u.v. wavelengths.

Polymer spheres were principally employed, but some tests were made using relatively monosize pollens, and a few made use of a powder having a range of particle sizes. Particle diameters are given in table 1.

Strong absorption of u.v. light occurred when either particles or marker solution passed the active region of the detector. This resulted in a clear delineation of the moment of passing by the registering of a pulse on the strip chart. Time for particle, or marker, transit through the capillary was taken as that from injection to the maximum of the u.v. absorption pulse; the flow rate was calculated from the transit time of marker solution or of the smallest particles, $0.176\ \mu\text{m}$ latex, these two times being indistinguishable in practice. Initially, the constancy of the flow, once set, was checked by collecting the liquid output for timed intervals. It was found to be consistent to within about $\pm 3\%$.

Table 1. Particle materials

Source	Material	Diameter (μm)
Dow Diagnostics	Polystyrene	5.7 ± 1.5
Dow Diagnostics	Polyvinyltoluene	2.020 ± 0.0135
Dow Diagnostics	Polystyrene	1.101 ± 0.0055
Dow Diagnostics	Polystyrene	0.822 ± 0.0043
Dow Diagnostics	Polystyrene	0.481 ± 0.0018
Dow Diagnostics	Polystyrene	0.312 ± 0.0022
Dow Diagnostics	Polystyrene	0.176 ± 0.0023
Duke Standards	Polystyrene	$18 \pm 1.3\%$
Duke Standards	Polystyrene	$9.8 \pm 1.1\%$
Duke Standards	Polystyrene	$5.1 \pm 1.2\%$
T. R. Stemen Laboratories	Paper mulberry pollen	12-14
T. R. Stemen Laboratories	Ragweed pollen	19-20
T. R. Stemen Laboratories	Pecan pollen	45-50
Barton Mines Inc.	Garnet	95% between 10 and 1

RESULTS

The injection of particles into the capillary tubing resulted, when the particles completed their transit and entered the u.v. detector, in a quite sharp peak on the recorder chart when the particles were monosize and a broader peak if not of one single size. Two peaks were obtained when two materials having different size particles were mixed before injection. No significant influence on transit time for either size could be detected because of the presence of the other. The peaks were separate if the materials were nearly monosize and considerably different in size; otherwise, the peaks were likely to be partially fused. Two-particle mixtures in marker solution produced either three separate peaks or three partially fused peaks, depending on the relative size and size spread among the particles. Garnet, having particles distributed in size, gave a broad peak; the peaks were generally skewed toward the finer sizes. Peak broadening increased even with monosize particles as size diminished.

To confirm that the recorded peaks actually corresponded to distinct particle sizes, individual liquid drops were collected as they emerged from the u.v. detector outlet and examined microscopically. Figure 1 is a recording from the detector of an initial mixture of $9.8 \pm 1.1\%$ and $2.020 \pm 0.0135\ \mu\text{m}$ spheres after passage through 91.4 m of $254\ \mu\text{m}$ i.d. tubing. Figure 2 shows

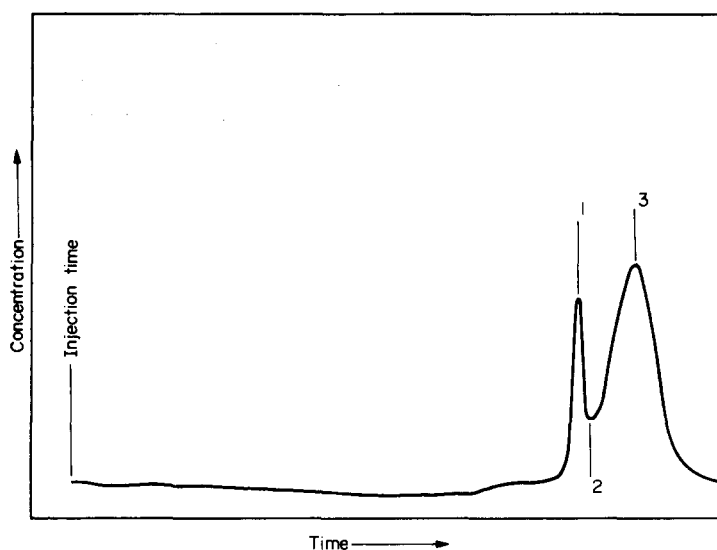


Figure 1. Particle segregation test.

micrographs of the particles corresponding to the three points identified on figure 1. Peak broadening with decrease in particle size as noted above, is clearly evident in figure 1.

Tables 2 and 3 give transit time data for particle materials carried in methanol through 91.4 m of 254 μm i.d. tubing at various flow rates. Reynolds numbers, $d\bar{v}\rho/\mu$ where d is capillary diameter, \bar{v} the mean liquid velocity, and ρ and μ liquid density and viscosity, respectively, ranged from 80 to 325 for the conditions indicated. These data plot reasonable straight lines on semilog graphs. Other results using 91.4 m of 254 μm i.d. tubing are presented as semilog graphs by figures 3 and 4; methanol was the carrier liquid in figure 3 and water in figure 4. Table 4 gives data for 508 μm i.d. capillaries of 88.4 and 201.2 m in length using methanol as the carrier.

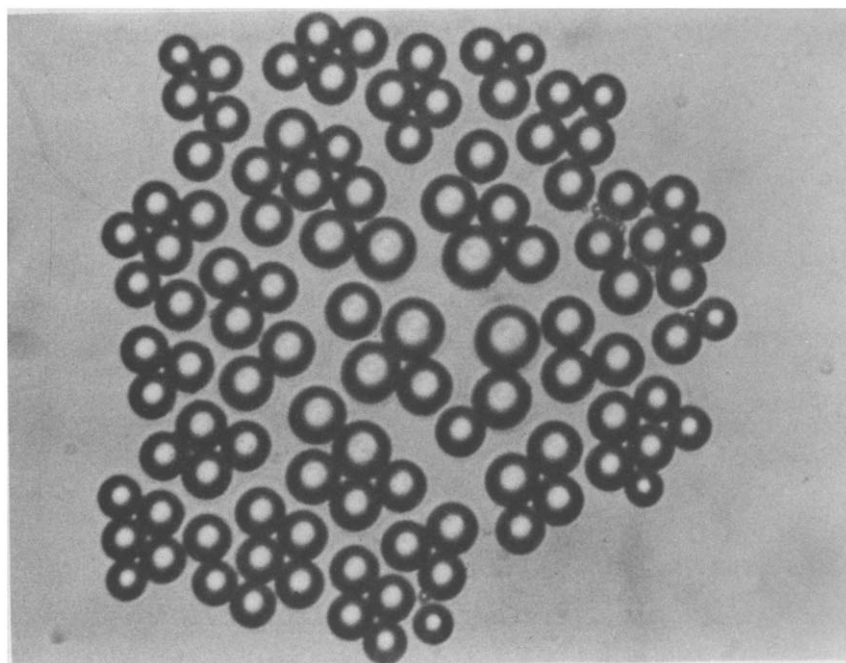


Figure 2a. Photomicrograph of Fraction 1.

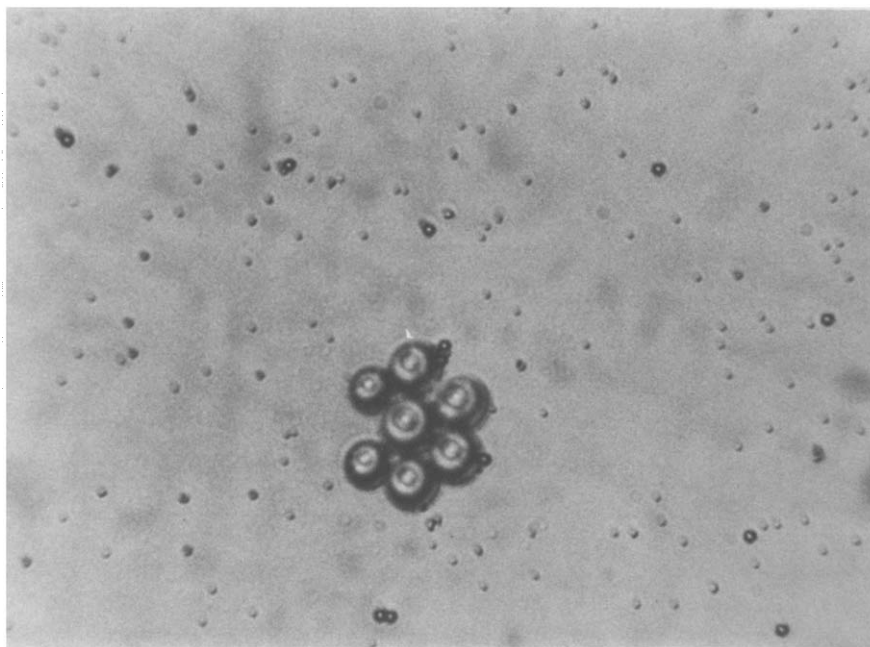


Figure 2b. Photomicrograph of Fraction 2.

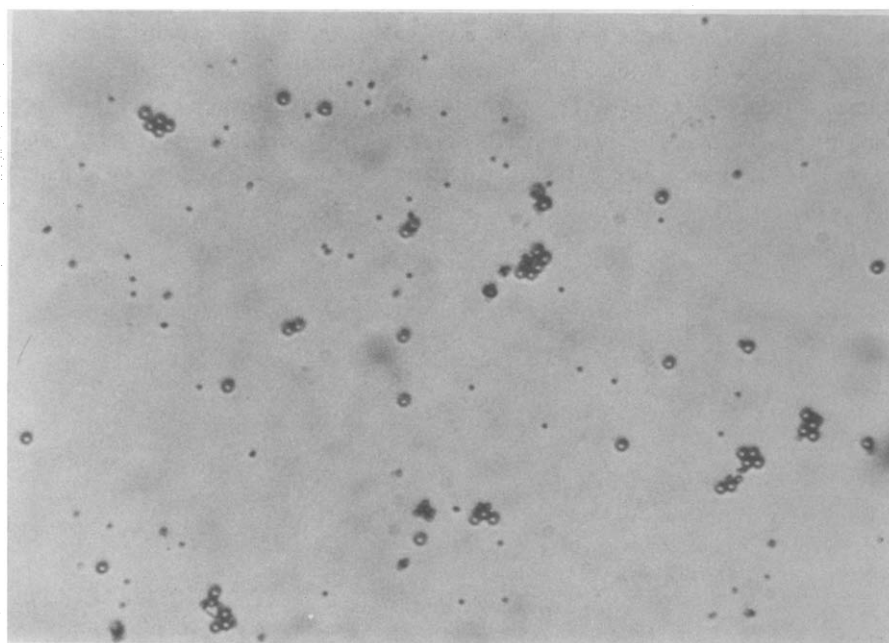


Figure 2c. Photomicrograph of Fraction 3.

Table 2. Measured transit times for pollens using methanol and a 91.4 m long capillary of 254 μm internal diameter

Pollen diameter (μm)	Time for particles to emerge at a flow rate of 1.14 ml/min (min)
12-14	3.33
19-20	2.60
45-50	2.42

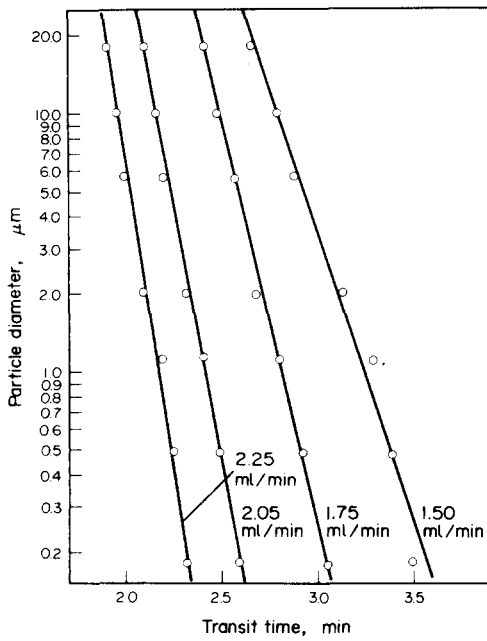


Figure 3. Particle diameter vs transit time: carrier liquid —methanol.

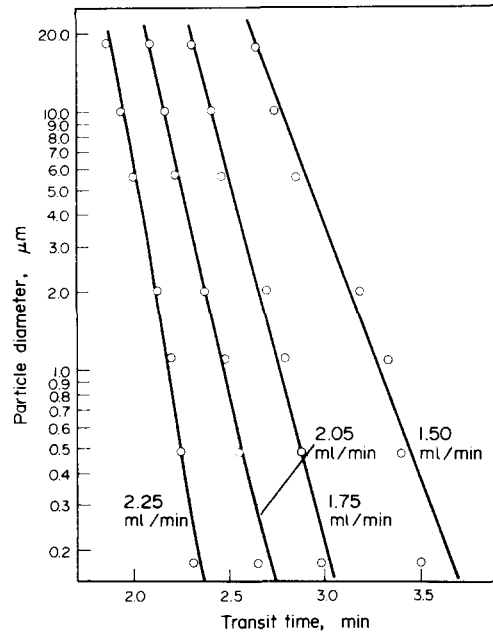


Figure 4. Particle diameter vs transit time: carrier liquid —water.

Table 3. Measured transit times for latex particles using methanol and a 91.4 m long capillary of 254 μm internal diameter

Particle diameter (μm)	Time for particles to emerge at flow rates (ml/min) of									
	0.69 (min)	0.89 (min)	1.09 (min)	1.14 (min)	1.32 (min)	1.55 (min)	1.78 (min)	2.01 (min)	2.22 (min)	2.57 (min)
0.176	6.75	5.20	4.27	—	3.50	2.98	2.60	2.30	2.08	1.80
0.312	6.75	5.08	4.13	—	3.42	2.93	2.55	2.28	2.03	1.77
0.481	6.73	5.12	4.40	4.08	3.43	2.87	2.50	2.20	2.00	1.72
0.822	6.60	4.85	3.97	4.03	3.28	2.83	2.48	2.20	1.98	1.72
1.101	6.42	4.83	4.00	—	3.60	2.75	2.40	2.17	1.97	1.68
2.020	6.08	4.92	3.80	3.72	3.30	2.63	2.33	2.07	1.87	1.62
5.70	6.00	4.88	3.35	3.41	3.20	2.53	2.22	2.03	1.80	1.60

Table 4. Transit time for particles using methanol and two lengths of capillary of 508 μm internal diameter

Particle Identification	Time for particles to emerge at flow rates (ml/min) of					
	88.4 m Capillary			201.2 m Capillary		
	5 (min)	7.5 (min)	10 (min)	5 (min)	7.5 (min)	10 (min)
0.481 μm Latex	3.58	2.39	1.82	8.17	5.47	4.04
1.101 μm Latex	3.52	2.35	1.78	8.16	5.38	4.00
9.8 μm Latex	3.23	2.18	1.69	7.48	5.21	3.96
19–20 μm Pollen	3.15	2.12	1.58	7.26	5.02	3.56

DISCUSSION

Liquid moving in laminar flow, Reynolds number < 1800 , through a cylindrical passageway is well known to assume a parabolic profile with the greatest velocity at the center and diminishing to zero as the wall is approached. That particles pass through a capillary more rapidly than does the liquid, which moves at the mean velocity, clearly shows that particles must, in general, assume flow positions near the tube center where they can partake of the higher-than-average velocity. Moreover, the larger the particles the nearer the center they must travel since the larger particles always precede the smaller ones.

Radial displacement of particles flowing inside tubes has been known for many years. In 1836 Poiseuille noted the existence of a corpuscle-free region near the walls of capillaries through which blood was flowing. Others have observed that a rigid sphere released near the wall of a flow channel moves away from the wall with a velocity proportional to its size and have commented on the existence of regions of low concentration both near capillary walls and at the center (Orr 1966).

Quantitative evaluation began with the study of Segre & Silberberg (1961, 1962). These investigators found a suspension of neutrally buoyant spherical particles flowing through a constant diameter tube of circular cross section became inhomogeneous with the particles concentrated in an annular region about the tube center. The equilibrium position for these particles was found to be very near 0.6 of the tube radius measured from the axis; it was attained independent of the initial particle lateral location. The phenomenon was termed the "tubular pinch effect". These findings were subsequently confirmed by others. Most notably, Jeffrey & Pearson (1965) repeated the lateral migration tests finding neutrally buoyant particles to move away from both the tube wall and the tube axis to establish stable flow positions at about 0.68 of the tube radius from the axis.

Taking measured particle and liquid velocities and the equation for the parabolic liquid velocity distribution for laminar flow in a circular tube, e.g. Bird *et al.* (1960), the effective axial position at which the particles employed here must have flowed can be readily calculated. Some of these numbers are given in table 5. They agree quite well with previously cited values although the particles do not precisely meet the neutrally buoyant criterion.

Table 5. Calculated flow position and mean velocity for typical particles when the mean liquid velocity was 57.5 cm/s

Particle diameter (μm)	Mean particle velocity (cm/sec)	Radial distance from axis/tube radius
18	74.5	0.570
5.7	69.2	0.625
2.020	65.5	0.650

Most previous proposed descriptions for the flow phenomena under consideration have begun with the Rubinow-Keller (1961) equation giving the lift force on a spinning, translating sphere in an unbound fluid at rest. The resulting "spin-slip" force in some treatments is such as to drive particles toward the tube axis. A "shear-slip" force as described by Ho & Leal (1974) would, on the other hand, force particles in the direction of increasing shear, i.e. toward the wall. The magnitude of both these forces would depend on the particle-to-tube dimensional ratio. A combined solution identifying a balance point has not been obtained as far as these researchers are aware. Nevertheless, capillary hydrodynamic chromatography would seem to offer promise for particle size analysis just as does column hydrodynamic chromatography.

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