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Particle Chromatography Using Naphthalene as a Host

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Abstract

Separation of metal and charcoal particulate mixtures suspended in naphthalene has been studied by accelerated directional solidification of the naphthalene, using the vertical Bridgman (VB) technique and tilt rotation zone melting (TRZM). In VB the separation was limited to monolayers of particles resting on the interface. An extent of separation ranging up to 68% was obtained by a single TRZM pass. However, the near-perfect separations thought to be possible were not obtained because of catastrophic trapping of particles in irregular mixed bands. Trapping, and perhaps separation as well, is enhanced by the presence of a large gas bubble sweeping the freezing interface (due to tube rotation).

INTRODUCTION

In a previous paper (*1*) it was shown that mixtures of particles suspended in a host liquid can sometimes be separated by directional solidification of the liquid at a steadily increasing rate. If all goes well, this results in particles of different types appearing in separate bands within the solidified liquid. Thus the name, "particle chromatography." Shih and Donaghey (*2*) showed that a separation into bands may alternatively

be attained by zone melting at constant velocity with multiple zone passes. We report here on many experiments performed to elucidate the influence of operating parameters on the separation attained using molten naphthalene as a host liquid (*3*).

EXPERIMENTAL

The experiments are described in detail elsewhere (*3*). Two techniques were employed—the vertical Bridgman technique (VB) and tilt rotating zone melting (TRZM). In both techniques the suspension was contained in a Pyrex tube. The freezing rate was gradually accelerated either by manual or automatic advance of the speed control.

In the VB technique a Nichrome wire resistance heater was placed around the top part of the tube (*4*). The 10-mm i.d. sample tube was lowered out of the heater, causing solidification to proceed upward. The particles rested on the freezing interface which was concave so as to avoid trapping at the tube wall (*5*).

Figure 1 shows a schematic daigram of the TRZM apparatus. The air jacket was added so as to avoid drafts, which had been observed to cause fluctuations in the freezing rate. The tubular condenser was added in order to prevent the interface from becoming concave as in our previous experiments (*5*), which it was thought would have caused the particles to accumulate at the center of the interface and reduce the mixing or tumbling action of the particles. In preparing the 13- or 22-mm o.d. sample tube, the naphthalene was purified and gas removed by a VB run, discarding a portion of the melt unfrozen. The particles were initially near the bottom of the tube and tended to move along with the zone. Unlike our previous results (*5*) using a horizontal rotating tube, it was found that little or no particle trapping occurred with a horizontal tube, even up to a zone travel rate of 6 cm/hr. We are now convinced that the trapping in our previous experiments (*5*) was enhanced by the large ($\sim 1/2$ of the zone) gas bubble present in each zone. Because of our method of sample preparation, little or no gas was present in the zones of the experiments described here. The remaining gas was dissolved into the melt by raising the power to the heater and expanding the zone (sometimes breaking the tube). Since it is apparent that particles can only be trapped if they contact the freezing interface, subsequent experiments were performed with the tube tilted, causing the particles to tumble along the bottom freezing interface. For each run the rotation rate and tilt angle were adjusted to provide a steady tumbling action and good contact with the

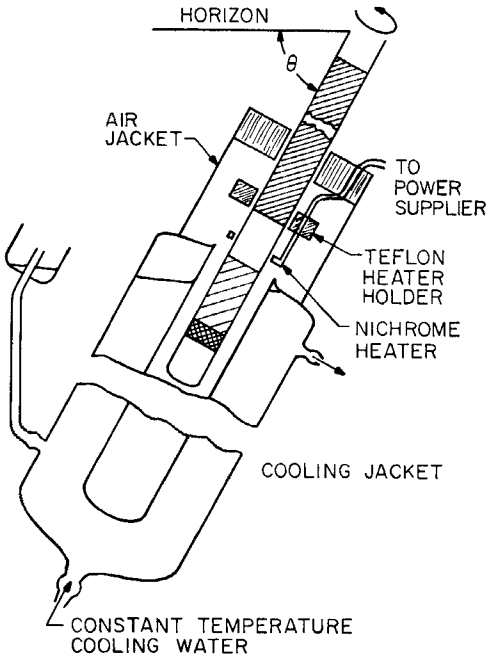

FIG. 1. Tilt rotating zone melter.

freezing interface. Tilt angles of 30, 35, 45, 57, and 60° and rotation rates from a few rpm to 20 rpm were tried.

Particles used were metal powders from Alcan and charcoal from Matheson, Coleman and Bell. Properties are summarized in Table 1. It was necessary to place the melt containing carbon in an ultrasonic cleaner in order to break agglomerates and disperse the particles. Three types of trapped particle bands were observed, with Type (2) being the most common:

(1) Discrete particles distributed fairly uniformly throughout the band.
(2) A thick dense layer of particles very near one another, or perhaps even in contact, preceded by a few independently trapped particles.
(3) Ridged bands, resembling a mountain range. (Only for Sb particles in TRZM.)

In TRZM the particle density sometimes varied markedly from one grain to another, as observed previously (*5*). Particle trapping appeared

TABLE 1

Size Analyses of Particles Used for Experiments (from data of suppliers)

Material	Grade	Control screen		Screen		
		Mesh	μm	Percent	Mesh	μm
Aluminum	MD201	200	74	92—	325	44
Antimony	MD301	325	44	99.9—	325	44
Cadmium	MD301	325	44	98—	325	44
Copper	MD165	150	105	53—	325	44
Copper	MD301	325	44	99—	325	44
Manganese	MD301	325	44	99.8—	325	44
Lead	MD201	200	74	98—	325	44
Nickel	MD101	100	149	39—	325	44
Silver	MD201S	100	149	70—	325	44
Charcoal			<13			

to generate new grains. The number of grains and gas bubbles produced decreased when fewer particles were used. After a run, two longitudinal cuts were carefully made with a diamond saw down opposite sides of the tube, to enable it to be removed without breaking the naphthalene. Analysis of trapped particles was made by first removing the naphthalene with a vacuum by placing the section in a vacuum flask immersed in a hot water bath. The particles were examined under the microscope and weighed. If one type of metal was used with carbon, the metal was dissolved in HCl and the remaining redried carbon weighed. If more than one type of metal was present, the solution was analyzed with an atomic absorption spectrometer. For each particle chromatography run, the extent of separation ξ was calculated using the bands in a combination to yield the largest possible value. The extent of separation was calculated by (*6*)

$$\xi_i = \frac{|n_{i1}n_{r2} - n_{i2}n_{r1}|}{n_i^0 n_r^0}$$

where n is the mass of the component, i is for the component under investigation, r is all other components, 1 and 2 are the desired collection of bands and/or residue (untrapped material), and the superscript 0 represents the total material (so $n_i^0 = n_{i1} + n_{i2}$). For a binary, $\xi_i = \xi_r$. If none of r is in Band 1, then ξ_i is just the fraction of i feed that is in 1.

VB RESULTS

In order to properly design the particle chromatography experiments, critical freezing rates* were first determined for each type of particle alone, as shown in Table 2. Then the feasibility of VB to separate multilayer particle mixtures was examined. In order to test whether the relative position of the particles influences their separation, different types of particles were placed layer by layer on the solidifying interface. It was found that if the particles were added to the bottom in a sequence of critical freezing rates from low to high, a separation could be produced, as shown in Table 3. If the particles were mixed, no detectable separation was obtained. This observation suggests that one should use either a smaller amount of particles (less than one layer thickness) or agitation so as to allow the particles a chance to touch the solidifying interface.

An experiment was performed to test the effectiveness of VB in separating a small amount of particles. The total weight of the particles was 0.0079 g, consisting of 0.00059 g Cd, 0.0011 g Cu, and 0.0052 g Ag.

TABLE 2

Critical Freezing Rates for VB

Particles	Critical freezing rate V_c (cm/hr)
0.00735 g Sb	1.356 to 1.42
0.00363 g Cd	1.2253
0.00143 g Fe	0.575
0.02511 g Pb	1.1278 to 1.534
0.005 g Mn	1.5963 to 2.5564
0.01 g Ni	1.2245
0.005 g Si	1.148
0.037 g Sn	1.263
0.2185 g Ag	0
Trace Ag	0.144
0.2199 g Cu	1.249
0.0977 g Cu	1.269
0.00543 g Cu	1.59
Very thick layer (~2000 μm) of Al	0.99
0.0645 g Al	1.98

*The critical freezing rate is defined as the freezing rate below which the particles are pushed indefinitely and never trapped, but above which at least some particles are eventually trapped.

TABLE 3

Effect of Particle Positions on the Degree of Separation in VBS

Run	Particles	Observations
BM3	Upper layer lead, lower layer silver	The silver particles were trapped immediately, and the lead particles were pushed up to their critical freezing rate of 1.55 cm/hr
BM4	Upper layer silver, lower layer lead	Both silver and lead particles were pushed up to 1.63 cm/hr and were then trapped without any separation
BM5	Mixtures of lead and silver	The silver particles were trapped as soon as they touched the solidifying interface, otherwise they were pushed by the lead particle layer. When the solidification rate reached the critical freezing rate of the lead particles, both silver and lead particles were trapped without showing any separation

This was less than one layer thickness. The particles were mixed before charging onto the solidifying interface. As shown in Fig. 2,* it was found that only silver particles were trapped separately at a solidification rate from 0.1 to 0.539 cm/hr. After the solidification rate was programmed up to 0.54 cm/hr in 7 hr, the trapping of silver particles stopped. Then the solidification rate was suddenly increased to 1.067 cm/hr, and cadmium, copper, and silver particles all began to be trapped. Every silver particle trapped in this stage was found to be agglomerated with copper or cadmium particles. No silver particle was trapped individually. Even though cadmium and copper particles were trapped in the same zone, most of the particles were trapped individually. This is because their critical freezing rates were very close. Thus this technique was able to separate a small amount of nonagglomerated particles.

TRZM RESULTS

In the tilt rotating zone melting technique, the frequency with which the particles contact the solidifying interface and the contact time ought to be very important factors in determining the critical freezing rate (or expressed differently, the freezing rate dependence of trapping prob-

*In the figures, where multiple bands appear the concentration of each component is given by the top line of the shaded portion for it, and not by the distance between the top and bottom line of its shaded portion.

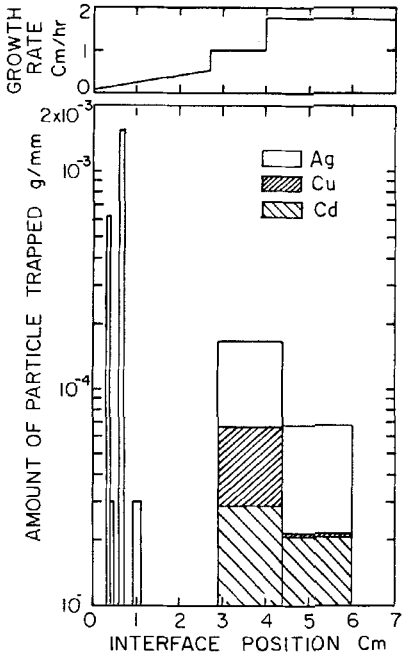

FIG. 2. Result of VB separation of monolayer of Ag, Cu, and Cd particles. Top: Tube lowering rate vs position. Bottom: Particle density vs position. $\xi_{Ag} = 0.43$, $\xi_{Cu} = 0.41$, $\xi_{Cd} = 0.21$.

ability). Thus suitable operating conditions had to be chosen to ensure good mixing and adequate particle–interface contact. Since the amount of particles might also effect the critical freezing rate, repeated experiments were performed with the same sample tube containing 0.24 g of Cu powder. After the particles were trapped, the molten zone was moved down slowly, permitting the entrapped particles to fall back to the lower section of the tube for the next experiment. The results are given in Table 4. It was found that a 57° tilt angle (measured from the horizon to the tube axis) and a rotation rate of around 4 to 6 rpm provided good mixing and adequate contact. For smaller tilt angles the particles settled on the lower corner of the tilted cylindrical zone, and thus the contacting time between the particles and the solidifying interface was too short. In run TRZM2 the particles were trapped over a freezing range of 1.75 to 2.8 cm/hr. This was because of the formation of bubbles on the solidify-

TABLE 4

Critical Freezing Rate vs Operating Conditions for Cu (all the runs were performed on the same sample tube, regenerated by moving the molten zone back to the bottom of the tube at the completion of each run)

Run	Tilt Angle[a]	Rotation rate (rpm)	Acceleration of solidification rate (cm/hr^2)	Range of solidification rate (cm/hr)		Displacement of solidifying interface (cm)	Critical freezing rate V_c (cm/hr)	Comment
				From	To			
TRZMA1	57	4.76	0.881	1.57	2.25	1.53	1.57; 2.25	Two bands trapped
TRZMA2	45	6.7	0.299	1.02	3.12	15	1.75; 2.01; 2.83	Three bands trapped with bubble
TRZMA3	45	7.15	0.815	3.12	6.38	13	>6.38	No trapping
TRZMA4	45	6.18	1.13	3.35	4.97	6.21	>6.21	No trapping
TRZMA5	45	6.5	1.07	0.11	3.33	13	>3.33	No trapping

[a] The tilt angle is the angle (in degrees) between the tube axis and the horizon.

ing interface. In other experiments performed under nearly the same conditions, only without bubbles, the particles were not trapped even at zone travel rates of 6.38 cm/hr. This indicates the importance of bubbles in explaining the differences between the present results and those of Kuo (*1*).

Since the critical freezing rate depends on the operating conditions, the critical freezing rate measured for TRZM is expected to be different from that measured for VB. Data for a tilt angle of 57° and a rotation of around 5 to 6 rpm are shown in Figs. 3 to 7 for Fe, Ag, Sb, Cd, and charcoal. It was found that the critical freezing rate measured by TRZM was larger than that measured by VB, as also found by Kuo (*8*) for horizontal rotating zone melting with a bubble.

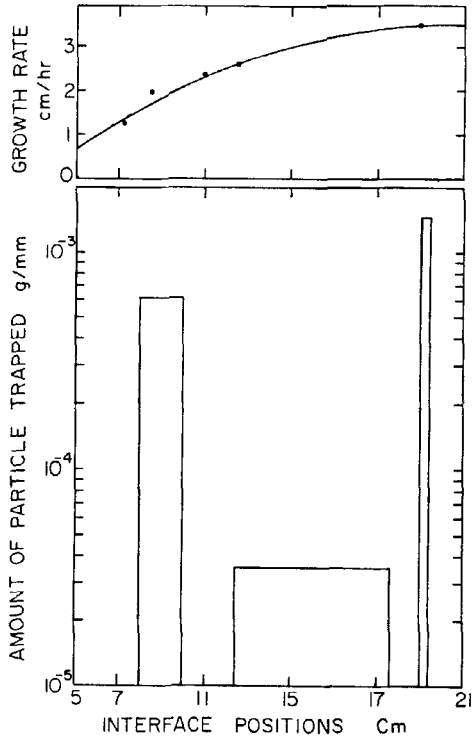

FIG. 3. Result of TRZM11 on 0.017 g Sb in 13 mm o.d. tube, 57° tilt angle, 6.52 rpm tube rotation rate. A few particles (~0.003 g) remained in the melt after 21 cm.

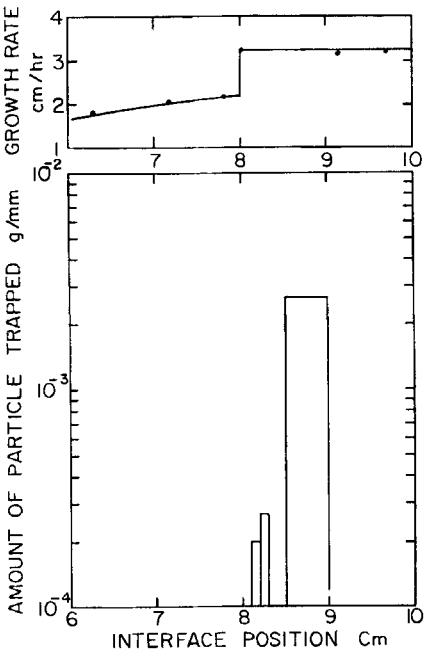

FIG. 4. TRZM16 with 0.013 g Cd in 13 mm o.d. tube, 57° tilt angle, 6 rpm tube rotation.

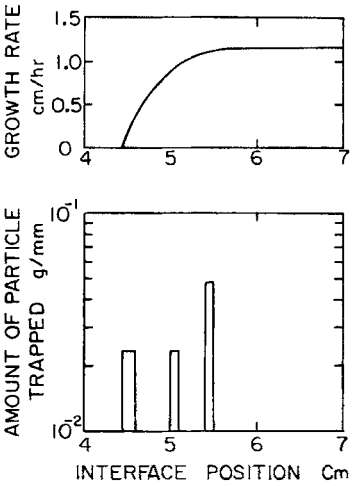

FIG. 5. TRZM31. 0.079 g Ag in 13 mm o.d. tube, 57°, 6 rpm.

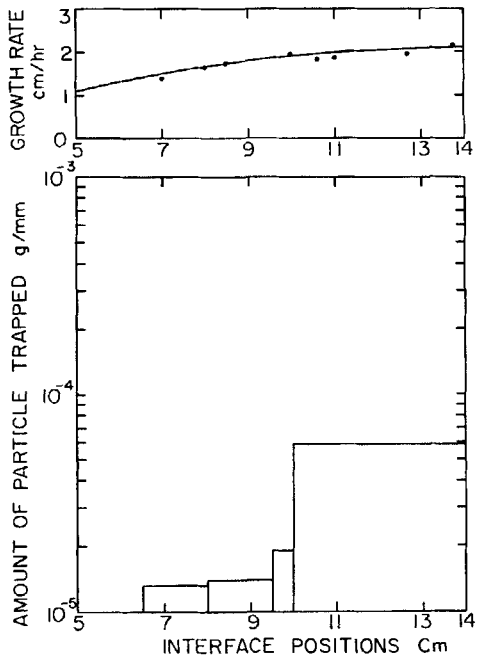

FIG. 6. TRZM32. 0.007 g Fe, 13 mm o.d. tube, 45°, 5.06 rpm. Tube broke at 14 cm with most particles not yet trapped.

Separation by TRZM of binary particulate mixtures of metal–metal and metal–charcoal powders was studied. The amount of the particles used in these experiments ranged from 2 to 100 times more than that separated by VB. The first three experiments (TRZM1 to 3) were performed without air and water jackets, and the solidification rate was found to fluctuate. After the molten zone was surrounded with an air jacket and the section of the sample tube below the molten zone surrounded by a water jacket (as shown in Fig. 1), the rate of change of solidification velocity was found to be smoother. The results are shown in Figs. 8 to 13, in which the solidification rate and the amount of entrapped particles versus position are plotted. The extent of separation does not appear to correlate with any experimental variable, including differences in V_c.

Experiments were also performed to see if TRZM can separate a Cu–Cd mixture, for which the critical freezing rates of the constituent

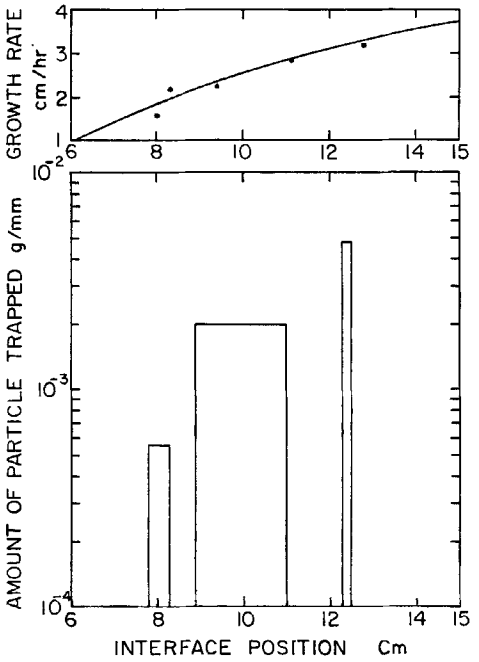

FIG. 7. TRZM33. 0.057 g C, 13 mm o.d. tube, 57°, 6 rpm. The majority of the particles were pushed to the end of the tube.

particles were so close that it could not be separated by VB. The operating conditions tried are listed in Table 5. No separation was obtained. It is interesting to note that the critical freezing rate V_c for mixtures was increased by increasing the rotation rate and decreasing the tilt angle, as observed when particles were of one type alone.

DISCUSSION AND CONCLUSIONS

The requirements for a particle chromatographic separation are:

(1) The trapping probability or frequency be significantly different for the different types of particles.
(2) Each particle has a fairly frequent opportunity to be trapped by the growing solid, i.e., it periodically contacts the freezing interface.

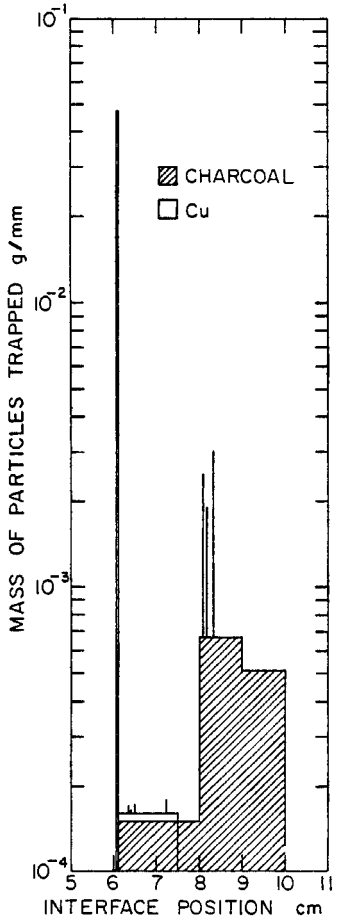

FIG. 8A. TRZM1. 0.0089 g Cu, 0.0078 g C, 13 mm o.d. tube, 57°, 4.6 rpm. $\xi = 0.68$.

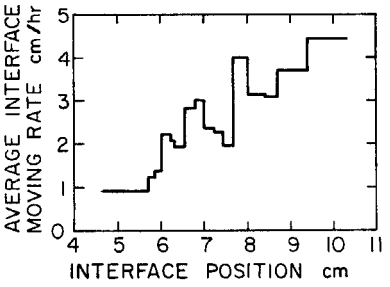

FIG. 8B. Freezing interface movement rate for TRZM1.

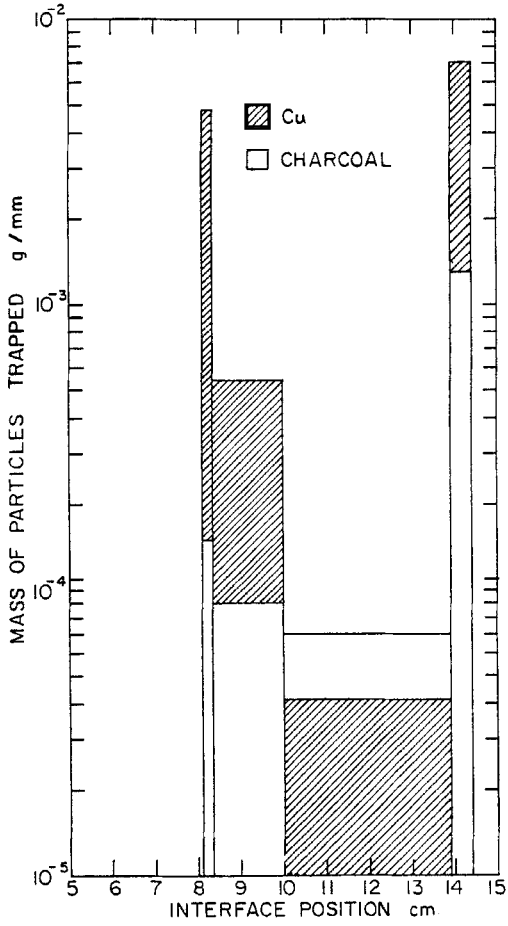

FIG. 9A. TRZM2. 0.020 g Cu, 0.0044 g C, 22 mm o.d. tube, 57°, 4.18 rpm. $\xi = 0.25$.

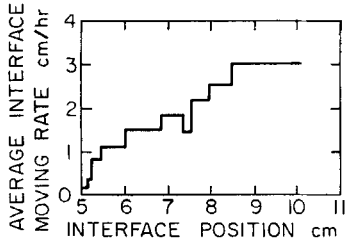

FIG. 9B. TRZM2.

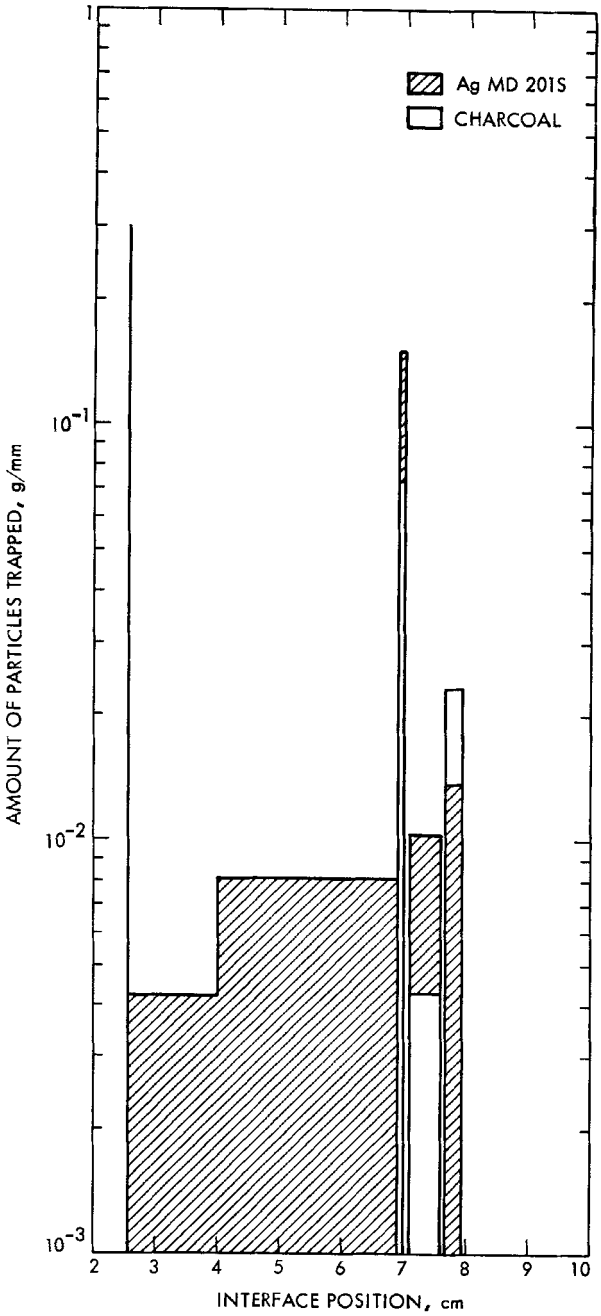

FIG. 10A. TRZM3. 0.69 g Ag, 0.18 g C, 22 mm o.d. tube, 57°, 5.03 rpm. $\xi = 0.65$.

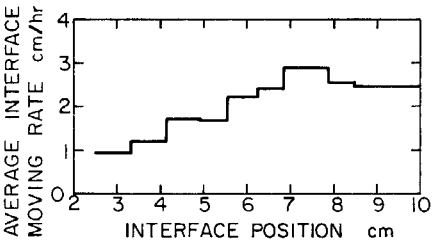

FIG. 10B. TRZM3.

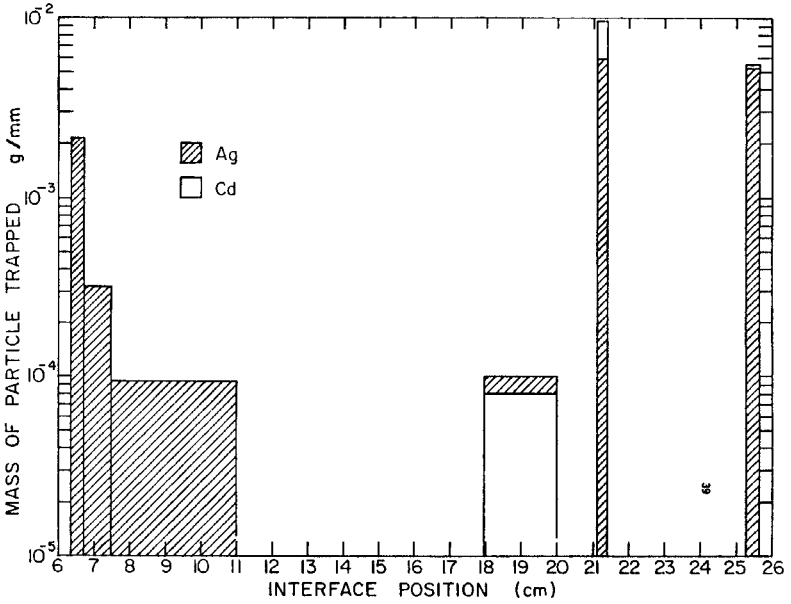

FIG. 11A. TRZM4. 0.048 g Cd, 0.049 g Ag, 13 mm o.d. tube, 57°, 14.1 rpm. $\xi = 0.27$.

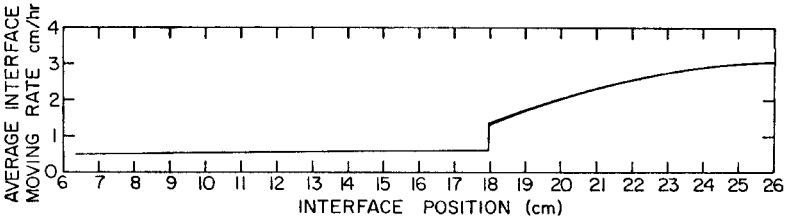

FIG. 11B. TRZM4.

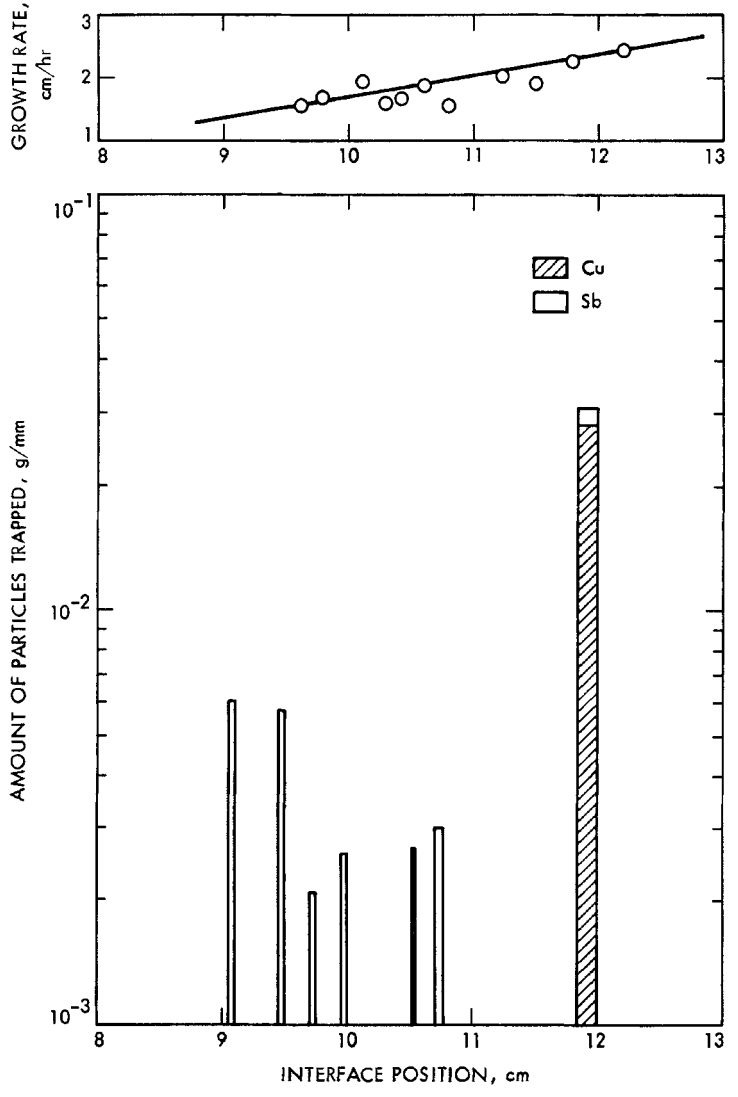

FIG. 12. TRZM14. 0.091 g Sb, 0.056 g Cu, 13 mm o.d. tube, 57°, 7.2 rpm. $\xi = 0.30$.

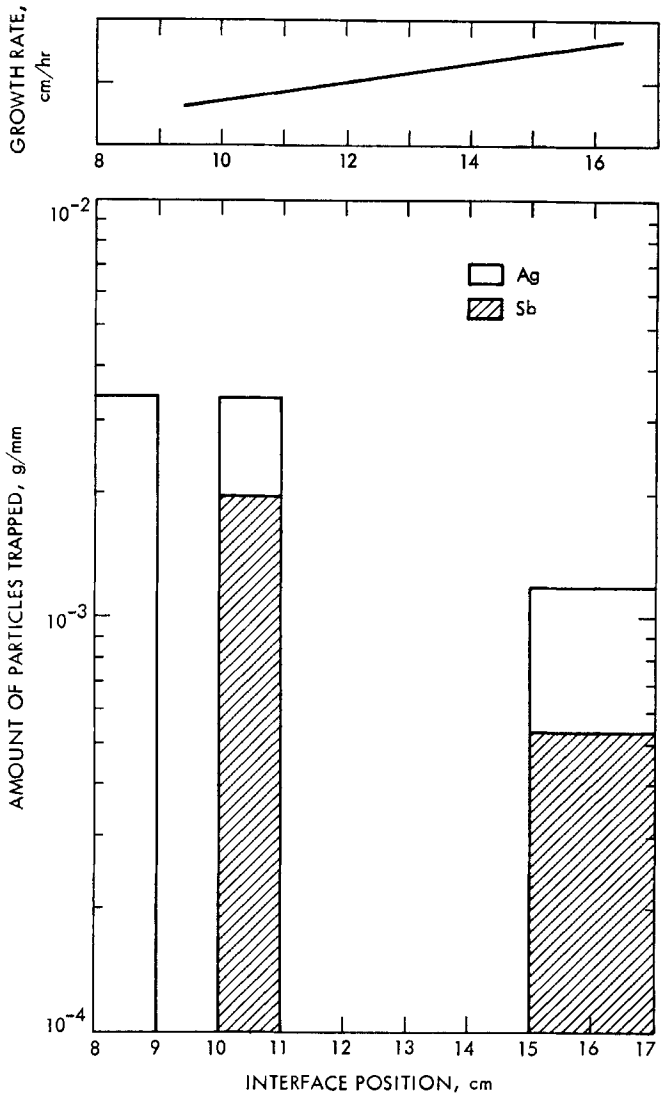

FIG. 13. TRZM30. 0.030 g Sb, 0.091 g Ag, 13 mm o.d. tube, 30°, 13 rpm. $\xi = 0.37$.

TABLE 5

Tilt Rotating Zone Melter Operating Conditions for Cu–Cd Mixtures (no separation obtained)

Run	Particle mass	Tilt angle	Rotation rate (rpm)	Critical freezing rate V_c (cm/hr)
TRZM18		57	13.1	2.1774
TRZM20		57	13.1	1.9674
TRZM21	0.02293 g Cu 0.02074 g Cd	57	4.07	1.4878
TRZM22	0.005 g Cu 0.00806 g Cd	57	4.07	1.198
TRZM23	0.02001 g Cu 0.00806 g Cd	45	10.13	2.8317
TRZM24	0.023 g Cu 0.021 g Cd	45	5.48	1.965

As one might expect, experiments on multiple layers in the vertical Bridgman technique confirmed the necessity for (2). Since one desires to separate more than a monolayer, it is then necessary to use a technique in which the particles are suspended or tumble on the interface. For this reason the rotating zone melting technique was selected.

Two differences were noted between the present experiments on tilt rotating zone melting and the previous results (*5*) using horizontal rotating zone melting. First of all, in the present experiments the particles were not trapped at all with a horizontal tube or sometimes even a slightly inclined tube, while trapping readily occurred in the previous experiments. The only apparent difference was the absence of a gas bubble in nearly all of the present experiments. Indeed, in a pair of experiments, one of which had a gas bubble, trapping occurred only in the one with a gas bubble. Probably the particles around the bubble are forced to contact the interface as the bubble sweeps along the interface because of tube rotation, while without a bubble they simply do not contact the interface for hydrodynamic reasons.

The second difference between the present and past (*5*) experiments is that the separations attained in the present experiments were much poorer. Perhaps we were simply fortunate in the preliminary experiments—beginner's luck. Or perhaps the bubble sweeping along the interface is essential for a good separation. Or perhaps the greater axial temperature gradient in the earlier experiments is helpful.

One striking feature of the present results is the trapping of particles

in irregular and nonreproducible bands, often with little separation occurring. Recent experiments at Clarkson College of Technology on coal fly ash particles have given identical results when naphthalene was used as a host material, but much better results when camphor was used (*7*). The principal difference between camphor and naphthalene is their tendencies to facet. Camphor, having a low entropy of fusion (*8*), never forms facets when solidifying. Naphthalene, on the other hand, sometimes forms facets at grain boundaries and forms faceted platelets when the melt is very impure or the solidification rate is very high. We have the impression that trapping in naphthalene is often a catastrophic event. Something causes one or a few particles to be trapped, which in turn enhances trapping of other particles. The initial triggering event could be a fluctuation in freezing rate. With a rotating tube this is not readily discerned, and the observations shown in the figures are too coarse to show any relationship with the bands. Perhaps a certain configuration of facetted grain boundary grooves forms which causes trapping of a few particles, although no preferential trapping in naphthalene grain boundaries was observed in our previous work (*1*). It did seem to us in the present research that the process of particle trapping generated additional grain boundaries. On the other hand, experiments with glass beads in naphthalene did not produce sharp bands (*9*).

Our TRZM work on Ag epitomizes the peculiar results obtained in this research. In run TRZM4 (Fig. 11) an Ag–Cd mixture was zoned at a constant rate which was above the minimum critical freezing rate for Ag (Fig. 5) and below that for Cd (Fig. 4). It was found that the amount of particles per unit length of the solid in the first band (from 6.3 to 6.6 cm) was 1.2×10^{-3} g/mm and contained 15% of the total silver. The amount of particles per unit length of the second band (from 6.6 to 7.45 cm) dropped to 2.3×10^{-4} g/mm and contained 5.2% of the total silver. That of the third band (from 7.45 to 11 cm) dropped still further to 10^{-4} g/mm and contained 6.7% of the total silver particles. Thus entrapment of Ag decreased with distance and finally ceased. Even though 72.3% of the silver was still left in the melt, the trapping virtually ceased in the section from 11 to 18 cm. The frequency of entrapment increased again when the solidification rate was raised to 1.15 cm/hr, and both cadmium and silver particles were trapped. The most likely explanation is that the trapping probability was not equal for all silver particles because of differences in shape and size. We have noted qualitatively that larger particles are pushed more readily than smaller particles, which is the reverse of results obtained without stirring or

tumbling of the particles (e.g., Ref. *10*). Recent experiments confirm this (*7*, *9*).

Thus particle chromatography has again been shown to be a promising technique for separation of particulate mixtures for analysis. However, difficulties have been encountered which must be solved by fundamental research before the technique can be applied to practical problems. Such research is underway at Clarkson.

Acknowledgments

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