Band Broadening Effects in Chromatography

Content Learning objectives:

1. Students will be able to explain how band broadening is related to flow rate.
2. Students will explain how the three components in the van Deemter equation affect bandwidth.

Process Learning Objectives:

1. Students will be able to describe relationships from a graph
2. Students will be able to sketch graphs of known relationships

Prior Knowledge:

Intermolecular forces
Introduction to Chromatography

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Band Broadening Effects in Chromatography

Consider this…

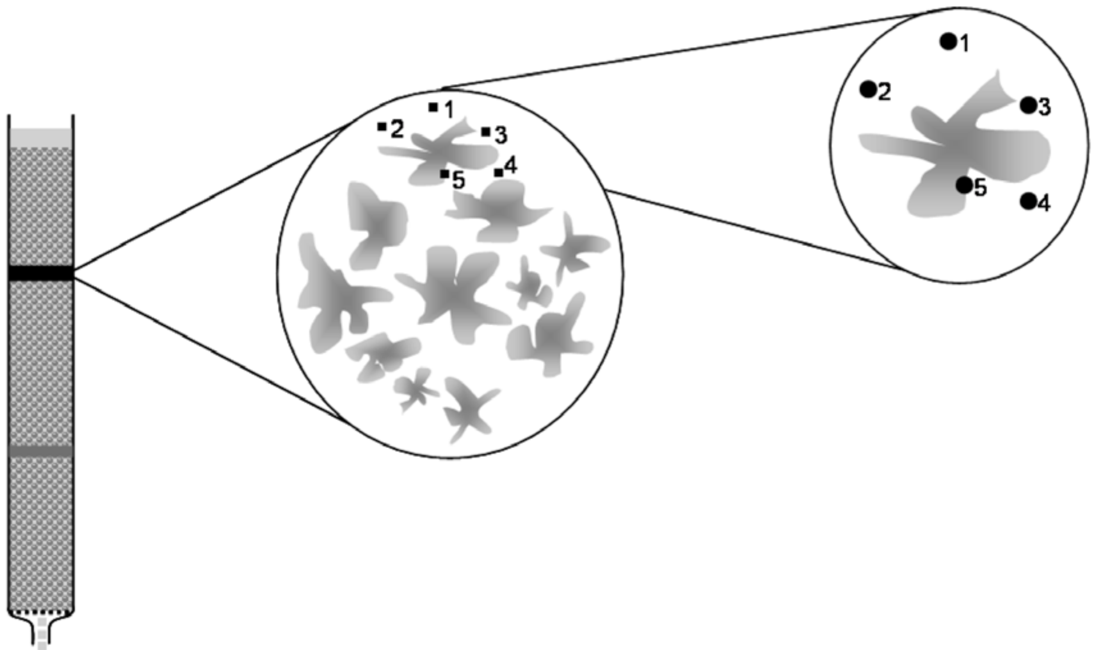


Figure 1: This is a snapshot microscopic view of 11 stationary phase particles in the packed column. Mobile phase is flowing from top to bottom. Only five (1-5) solute molecules are shown for simplicity. All the space between the stationary phase particles is filled with mobile phase, which is not shown.

Key Questions

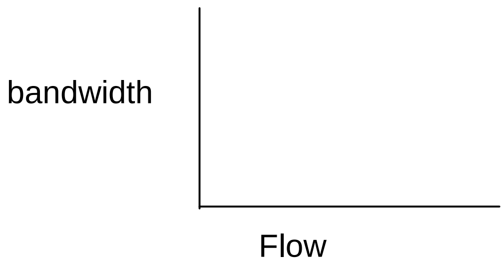
Multiple Paths

1. Consider particle 1 in the middle view. Each group member should draw a path for particle 1 to move through this section of the column.

2. Compare your results. Which path is shortest? Which path is longest?

3. What effect would the different paths have on the broadness of the peaks eluting from the column?

4, If the mobile phase flow rate increases, will the number of possible pathways change or will the particles move faster through the existing pathways? Based on this, sketch in a graph the relationship between bandwidth vs. mobile phase flow rate.



5. Write a proportionality between bandwidth and mobile phase flow rate u_x.

Mass Transfer

6. Consider particles 2 and 3. Partitioning to the stationary phase requires solute molecules to move towards stationary phase particles. This is called mass transfer. Which particle, 2 or 3, takes longer to reach the stationary phase particle?

7. As the mobile phase continues to travel through the column some particles, such as particle 3, become adsorbed at the surface of the stationary phase particle. Particle 2, since it has further to travel, may not reach the stationary phase particle before being swept past the stationary phase particle.

What effect will this have on the broadness of the peaks eluting from the column?

8. As you increase the flow rate, is it more or less likely that the solute particle will be swept past the stationary phase particle? Will this increase or decrease band broadening?

9. Assume that the relationship between bandwidth due to mass transfer and flow rate is linear. Write a proportionality between bandwidth (*w*) and mobile phase flow rate u_x.

Longitudinal Diffusion

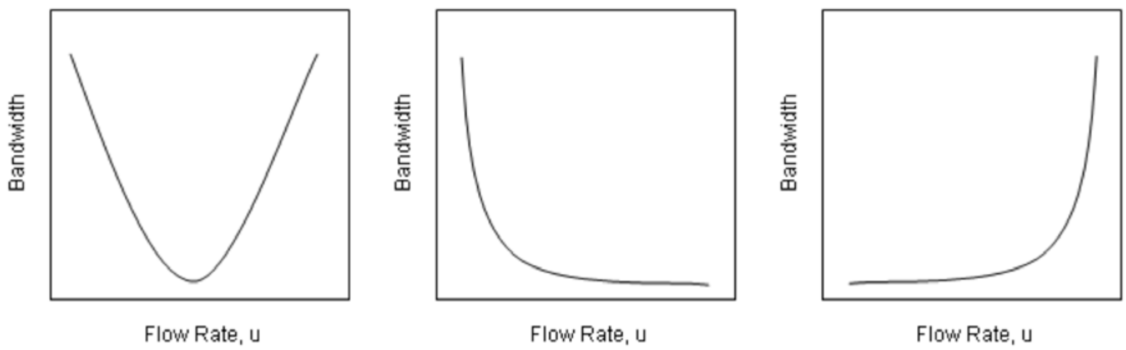
10. Consider particle 2. What is the most likely direction that particle 2 is traveling through the column?

11. If we stop the mobile phase from flowing, particle 2 will diffuse in the column. Draw arrows around particle 2 to indicate the possible directions it will move.

12. What effect will diffusion have on the broadness of the peaks eluting from the column?

13. Band broadening due to diffusion depends on flow rate. Will band broadening due to diffusion be more pronounced at slow or fast flow rates?

14. The relationship between the broadness of the peaks due to diffusion and mobile phase flow rate is represented by one of the following three graphs. Choose which of the three models represents this relationship. Explain your rationale. Write a proportionality between bandwidth due to diffusion and mobile phase flow rate u_x.



Consider this…

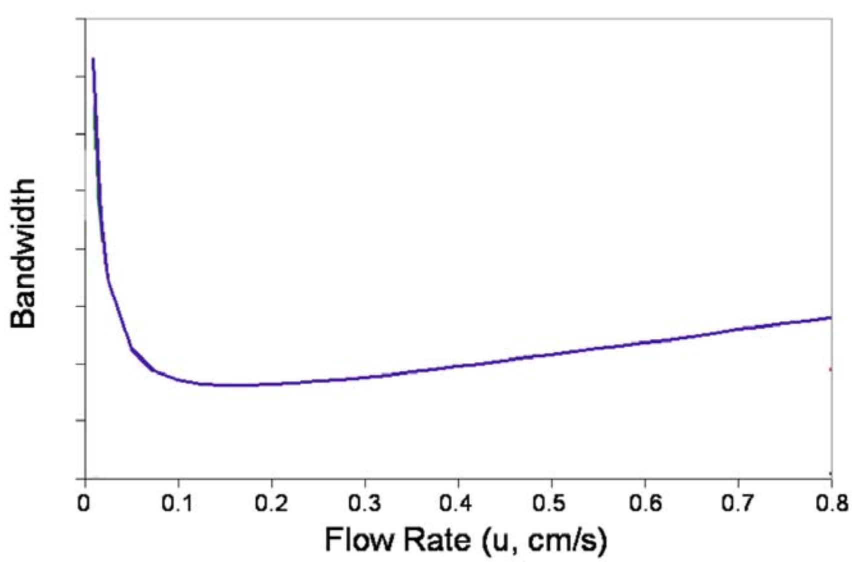


Figure 2: The graph shows the sum of the three effects on band broadening.

Key Questions

15. At low flow rates, which of the three processes (multiple paths, mass transfer, or longitudinal diffusion) is dominant?

16. At high flow rates, which of the three processes is dominant?

17. What flow rate would you use to minimize band broadening?

18. The overall relationship between band broadening and flow rate includes the three proportionalities developed above. These effects are additive. Write an overall equation expressing the relationship using constants A, B and C.

Applications.

1. The relationship between band broadening and flow rate is known as the van Deemter equation. What is the impact on band broadening (increase, decrease or no change) due to each van Deemter variable for each of the following conditions?

	Multiple Paths	Diffusion	Mass Transfer
Increase temperature			
Longer column			
Using a gas mobile phase instead of liquid			
Smaller particle stationary phase			

2. Below are van Deemter plots where the mobile phase is either a gas or a liquid and the y-axis is column efficiency, H, a quantitative measurement of band broadening. Predict which graph represents which mobile phase and explain your answer (graphs adapted from Figure 30-13 in Skoog, D. A., S. M. West, F. J. Holler, and S. R. Crouch. *Fundamentals of Analytical Chemistry*, 8th ed., Belmont, Ca:Brooks/Cole, 2004.)