Gas Chromatography Problem Solving and Troubleshooting

Question:

Column activity or contamination is the usual cause of my tailing phenol peaks. How can I determine which one is the cause of the tailing peaks?

Answer:

Column activity is primarily due to the presence of silanol (Si–OH) groups in a capillary column. The inner surface of the column tubing is the primary location for the silanol groups. For packed columns, the stationary phase support is the primary source of activity. Column contamination is usually caused by the accumulation of solid debris or high molecular weight compounds in the column. Select compounds can interact with the support, silanols, or contaminants, which results in peak tailing. Compounds containing hydroxy (–OH) or amine (–NH) groups are the most susceptible to this type of interaction; a few aldehydes may also exhibit peak tailing due to column activity or contamination. Phenols are very active and often exhibit peak tailing due to column activity or contamination.

There are a series of simple tests that can be used to indicate whether activity or contamination is a possible source of peak tailing. Unfortunately, most of these tests are not conclusive and can only be used to confirm activity or contamination as a possibility. Column test mixes can be used to measure column activity (1); they can be purchased from the column manufacturer or made in the lab. Peak tailing for some or all of the alcohols, acids, or amines in the test mixture is an indicator of column activity. However, column contamination often causes peak tailing of the active compounds also. Peak tailing for inactive compounds is indicative of problems with the injector, leaks, gas flow rates, or column installation; particles in the column may also cause peak tailing for inactive compounds.

Column activity, if present, usually affects the entire column (because every part of the column contains silanol groups), but column contamination is usually localized at the front of the column. Trimming or cutting 0.25–1.0 m from the front of a capillary column often removes the most contaminated portion. After trimming and reinstalling the column, the amount of peak tailing should decrease or disappear if contamination was the source of the problem. If the amount of peak tailing remains about the same, either column activity or severe contamination is responsible for the tailing. Cutting the front of a capillary column is analagous to repacking the front part (discolored portion) of a packed column.

When a temperature program is being used, the front portion of the column has the greatest influence on peak resolution and shape. Since column contamination is more severe in the front portion of the column, it has a large impact on the quality of the peaks. Instead of cutting off some of the front of the column, reversing the direction of the column (injector end into the detector and detector end into the injector) has the same overall effect. Then the most contaminated portion is at the back of the column where it has the least amount of influence on peak shapes. The column is still contaminated, but the contamination has little impact on the peaks. If the peak tailing is removed or reduced, contamination was the most likely cause. If the peak tailing is about the same, column activity is the most likely cause, but a severely contaminated column will generate the same results. There are several advantages to reversing a capillary column rather than trimming the front. The same amount of peak tailing in both column directions is a stronger indicator of column activity than the same result after trimming the column. Also, the column reversal test is nondestructive because a length of column is not removed. Disadvantages include the necessity for a complete column reinstallation and conditioning procedure, the moving of any semivolatile contaminants closer to the detector and potentially fouling the detector, and the fact that the test only works under temperature program conditions.

The purpose of *Chromatography Problem Solving and Troubleshooting* is to have selected experts answer chromatographic questions in any of the various separation fields (GC, GC–MS, HPLC, TLC, SFC, HPTLC, open column, etc.). If you have questions or problems that you would like answered, please forward these to the *Journal* editorial office with all pertinent details: instrument operating conditions, temperatures, pressures, columns, support materials, liquid phases, carrier gas, mobile phases, detectors, example chromatograms, etc. In addition, if you would like to share your expertise or experience in the form of a particular question accompanied by the answer, please forward to JCS Associate Editor, *Chromatography Problem Solving and Troubleshooting,* P.O. Box 48312, Niles, IL 60714. All questions/answers are reviewed to ensure completeness. The *Journal* reserves the right not to publish submitted questions/answers.

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If column contamination is indicated or suspected, solvent-rinsing a capillary column is the usual procedure to remove the contaminants (2). Only bonded and cross-linked capillary columns should be solvent-rinsed. Consult the column manufacturer or a reliable source if there is any question about rinsing a particular capillary column. If the peak tailing is eliminated with a column rinse, contamination will have been the source of the problem. If the peak tailing is about the same, column activity or contamination with very high molecular compounds (or any compounds not soluble in the rinse solvents) will have been the source of the problem. For contaminated packed columns, repacking the front portion of the column or baking out the column is the usual procedure. Baking out involves leaving the column at or near its upper temperature limit for 8 h or more (sometimes days). This is not recommended for capillary columns. Only a 1–2-h bakeout should be attempted. Longer times only reduce column life or irreversibly contaminate a capillary column.

Depending on the compounds, some contaminants are not removed by a solvent rinse procedure. In such cases, part of the column may be salvageable. Cut the column somewhere near the middle and test the original back portion of the column. Even if a solvent rinse had not been completely successful, the front part of the column would probably still be the most contaminated portion. The back half of the column is usually much cleaner than the front half and often exhibits satisfactory performance. Although the back half is substantially shorter than the original column, it may still provide adequate resolution. Also, it may make a good backup column or one suitable for another analysis.

It is often difficult to absolutely determine whether peak tailing of active compounds is caused by column activity or contamination. The various tests can help to indicate which problem is most likely, but it is easy to be misled.

References

1. D. Rood. Troubleshooting. *J. Chromatogr. Sci.* **34:** 96 (1996).
2. D. Rood. Troubleshooting. *J. Chromatogr. Sci.* **33:** 596 (1995).