Gas Chromatography Problem Solving and Troubleshooting

Question

I noticed a series of small peaks in my blank chromatograms. The mass spectra of these peaks appear to match the spectra for column bleed. I thought column bleed did not appear as peaks. Are these peaks column bleed? If not, why do their mass spectra look like column bleed?

Answer

The peaks are not column bleed. Column bleed is a continuous stream of stationary phase degradation products eluting from the column. Column bleed is a component of the baseline and not a series of peaks. Column bleed increases with temperature, especially at temperatures near the column's upper temperature limit. When temperature programming up to the upper temperature limit, a rise in the baseline at higher temperatures is the typical and most obvious sign of column bleed.

Most capillary column stationary phases are based on siloxane polymers. Although there are other types of stationary phases, polysiloxanes are definitely the most common. Polysiloxanes can be described as having a repeating silicon–oxygen backbone substituted with various side groups (i.e., methyl, phenyl, and cyanopropyl). At higher temperatures these very long chain polymers degrade into smaller lengths of the same repeating units that can elute from the column. These degradation products and their fragments comprise the mass spectra taken along the baseline (i.e., not on a peak).

Silicones are used in a large number of common household and consumer products. They are found in large amounts in many soaps, lotions, deodorants, pharmaceuticals, and similar products. Silicones are also used in lubricants, protective coatings, sealants,

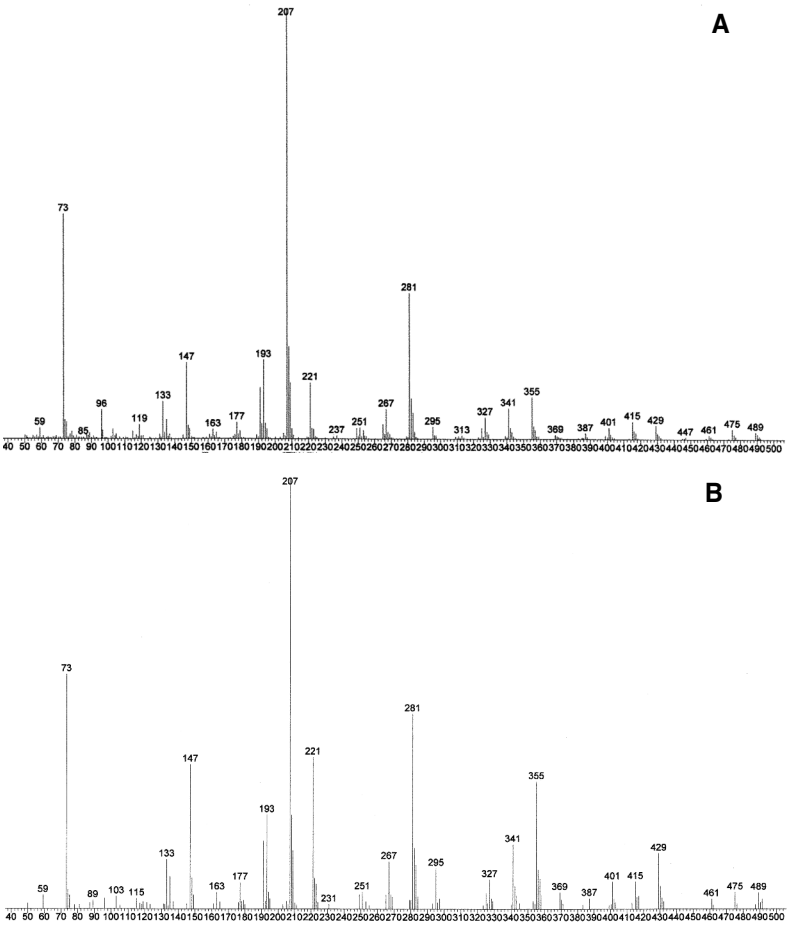

Figure 1. Mass spectra of column bleed and silicone septa: (A) 5% diphenyl–95% dimethylpolysiloxane stationary phase at 325°C and (B) injector septum extracted with methylene chloride.

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 it 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.

Dean Rood
Associate Editor

gaskets, o-rings, and related items. Because of their widespread presence in the environment, silicones are common sample contaminants. One of the most common sources of silicone contamination in GC systems are sample vial and injector septa. Many capillary column stationary phases and silicone septa are made from similar or identical materials. Repeated piercing of septa may generate small particles that become lodged in an injector liner or contaminate a sample. When in contact with solvent or at high temperatures, the particles leach materials very similar or identical to the degradation products (i.e., bleed) of many columns. Because the chemical structures are very similar, it is easy to misidentify the contaminant mass spectra as column bleed mass spectra. Figure 1 shows an example of this situation. Figure 1A is the bleed spectra for a 5% diphenyl–95% dimethyl polysiloxane stationary phase (i.e., DB-5, HP-5, Rtx-5, and SPB-5) at 325°C. A methylene–chloride-extracted injector septum analyzed by GC–MS results in a chromatogram with a series of regularly spaced peaks with nearly identical mass spectra (Figure 1B). This extract is representative of septum bleed. The mass spectra differ in only minor variations in their mass abundances. It is very easy to confuse the two mass spectra.

Because of normal variances in column bleed and septa mass spectra, it is extremely difficult to distinguish between the two based on their mass spectra alone. Other clues such as the appearance of the chromatogram (i.e., peak-free baseline versus peaks) or visual inspection are necessary to identify the actual source of the mass spectra. The series of small peaks in the blank chromatogram strongly points to septum bleed and not column bleed as the primary source of the mass spectra.

Acknowledgments

The mass spectra are courtesy of Angelica Reese of Agilent Technologies.