Gas Chromatography Problem Solving and Troubleshooting

Question:

Sometimes a series of peaks appear in my chromatograms. A mass spectral library search indicates that these peaks are silicon-based compounds related to the column's stationary phase. Are these peaks column bleed? How do I prevent or eliminate them?

Answer:

The peaks in your chromatogram are not caused by column bleed (Figure 1). Column bleed does not appear as peaks but as a rise or increase in the baseline at elevated column temperatures (1). The baseline rise in Figure 1 starts around 20 min, continues to rise until the final column temperature is reached around 25 min, and then levels out as the column temperature is held constant. This is the portion of the chromatogram that results from column bleed. A mass spectral scan at 28 min, where the column bleed is the highest, results in the mass spectrum shown in Figure 2A. This is a typical mass spectrum for a 100% methyl substituted silicone stationary phase such as the one used to generate the chromatogram in Figure 1. It is virtually the same column bleed mass spectrum that is obtained for a 5% phenyl–95% methyl substituted silicone. The most notable features are the masses at *m/z* 73, 207, and 281. These masses correspond with the stable degradation products of high methyl content silicone stationary phases. The most abundant mass is always *m/z* 207; *m/z* 73 and 281 are usually the next most abundant. The abundance of *m/z* 73 may vary and often range from the second to the fourth most abundant mass in the column bleed mass spectrum. Often *m/z* 355 and 427 are observed; however, their abundances are usually very low. The upper scan range for the chromatogram in Figure 1 was *m/z* 350, thus these higher masses are not observed.

Upon comparing the column bleed mass spectrum with a mass spectrum that corresponds to one of the chromatographic peaks, many similarities are evident (Figure 2B). Many of the same masses are present; however, their relative abundances are very different. Although the major masses are the same, the differences in their relative abundances eliminate column bleed as a possible source of these interferences (in addition to the fact that column bleed is not visible as peaks). It is easy to see how the peak mass spectrum can be confused with the column bleed mass spectrum. The mass spectrum of the other peaks in the chromatogram is the same as shown in Figure 2B. The regular spacing of the interference peaks indicates that the contaminants are compounds most likely present as a homologous series. Silicon-based homologous series include materials from silicon-based lubricants, GC septa, and the liners or septa of vial or bottle caps. These compounds are introduced into the column and, upon eluting from the column, appear as peaks and baseline drift or noise in the chromatogram. These contaminants can be present in the carrier gas flow path in the GC (e.g., gas lines, traps, regulators, valves), in the injected sample, or in any item that comes in contact with the sample, such as syringes, pipettors, or containers.

Hydrocarbons are another common contaminant encountered in the GC system. Like many silicon contaminants, they usually appear as a series of regularly spaced peaks corresponding to a homologous series. Hydrocarbons have a characteristic mass spectrum distinguished by a series of masses that are 14 units apart (Figure 3A). Usually the masses are most abundant in the *m/z* 40–90 range; *m/z* 43, 57, 71, and 85 are the most common. Lubricants, pump oils, hand lotions, improperly cleaned copper and stainless steel tubing, expired gas traps, and inexpensive gas regulators are some of the most common sources of these contaminants.

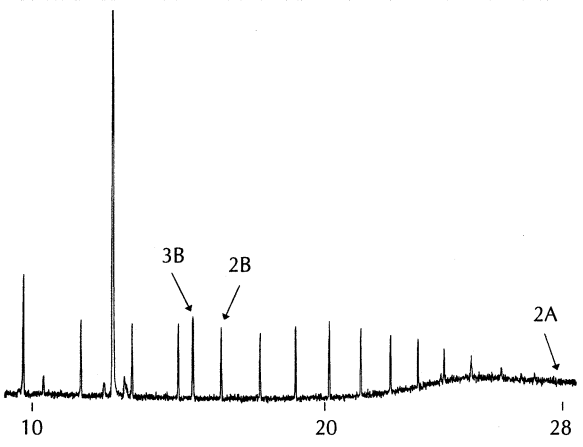

Figure 1. Chromatogram showing contaminant peaks. The labels correspond to the figure number illustrating the respective mass spectrum. Conditions: DB-1 column (30 m x 0.25-mm i.d., 0.25-µm film thickness), splitless injector (250°C, 0.5-min purge activation time), MS detector (320°C transfer line, *m/z* 50–350 full scan), helium carrier gas (30 cm/s), 50°C column temperature for 0.5 min, 50–125°C at 25°C/min, 325°C for 5 min, 50-ng/µL sample (mescaline in methanol).

Besides the peak of interest at 12.70 min, there is an additional peak in Figure 1 that falls out of the evenly spaced series of peaks. The mass spectrum corresponding to this peak shows a dominant mass at *m/z* 149 (Figure 3B). This is a typical mass spectrum for a phthalate. Phthalates are another common contaminant; they most often originate from plastics. If the sample or any of its components have come into contact with any plastic, phthalate contamination is always a possibility.

Using clean glassware and high-quality septa and caps and minimizing sample contact with plastics and oils are some of the techniques that can be used to reduce these types of contamination problems. In some cases, the contaminants can accumulate in the GC system; the most common site is the injector. There are cooler regions of the injector, such as the gas lines, where contaminants can collect. Flowing carrier gas or solvent vapors from future injections of samples can

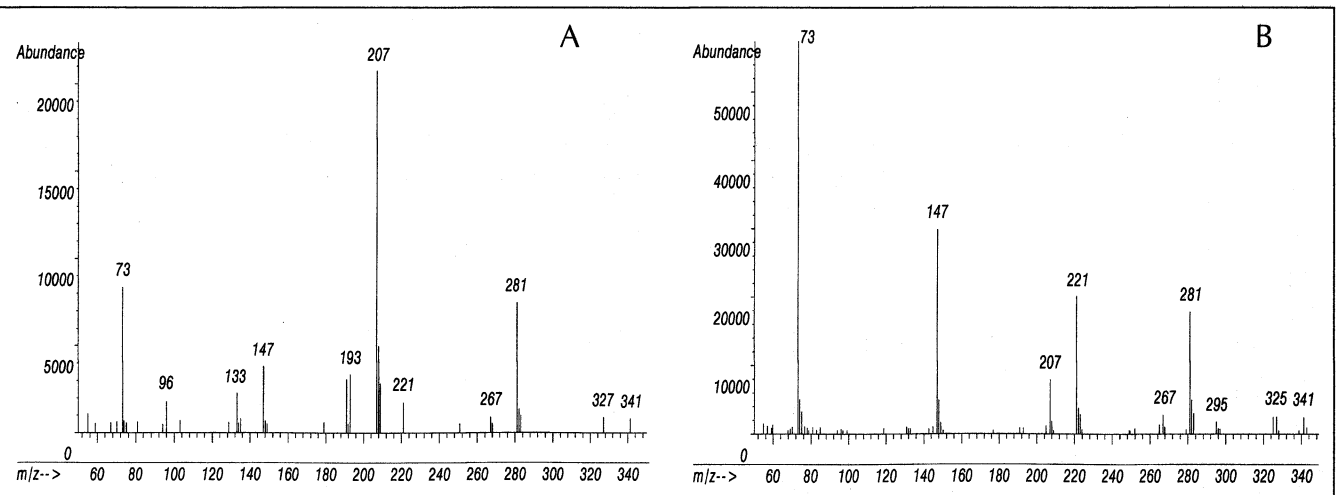

Figure 2. Mass spectra. (A) Column bleed, baseline at 27.95 min. (B) Unknown silicone compound peak at 16.41 min.

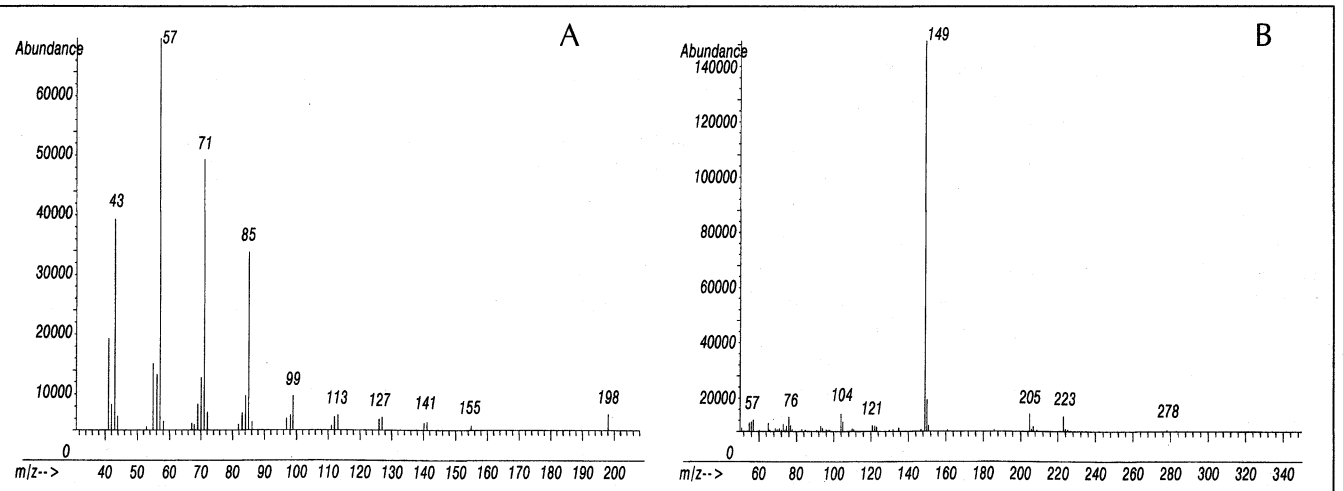

Figure 3. Mass spectra. (A) Typical hydrocarbon mass spectrum. (B) Unknown phthalate peak at 15.44 min.

transport these contaminants into the column. These contaminants can then elute from the column and interfere with the peaks in the chromatogram. If the contaminants are silicon-based, their mass spectra are often very similar to column bleed mass spectra.

Reference

1. D. Rood. Gas chromatography problem solving and troubleshooting. *J. Chromatogr. Sci.* **33:** 347 (1995).

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.

Dean Rood
Associate Editor