Gas Chromatography Problem Solving and Troubleshooting

Question:

The bleed in my column increased to an unusable level about 5 times faster than in the past for the same column. When this column was new, it was accidentally heated at 25°C above its upper temperature limit for 1 h. Would this overheating be the cause of the rapid increase in the bleed level?

Answer:

Exceeding a column's upper temperature limit by 25°C for a short period of time, such as for 1 h, would not be solely responsible for the rapid onset of column bleed. Upper temperature limits are set by the column manufacturer and are usually based on the amount of column bleed deemed acceptable by that column's manufacturer. There may be other factors involved in setting the upper temperature limits, but column bleed is usually the most influential. For most columns, the upper temperature limit is quoted as two numbers (e.g., 280/300°C). The lower value is called the isothermal temperature limit, and the column can be maintained at this temperature for prolonged periods of time. The second value is the program temperature limit. The column can be temperature programmed up to this value and held at that temperature for a short period of time. Although different times are often quoted, a maximum time limit of 10–30 min is typical. Column bleed at the program temperature limit is usually substantially higher than at the isothermal temperature limit.

Exceeding the upper temperature limit of a column does not result in immediate and substantial column damage. Provided there is carrier gas flow in the column and the oxygen concentration in the carrier gas is low (< 2 ppm), the amount of stationary phase damage is relatively small. Although it is best not to overheat any column, short term exposure of a column to temperatures 25–50°C above its limit rarely results in any significant damage to the column. Long times (> 1 h) at temperatures well above the upper limit results in noticeable column lifetime reduction, since substantial damage of the stationary phase occurs. In general, polar stationary phases are more sensitive to thermal damage than non-polar phases. For example, polyethylene glycol-based stationary phases exhibit signs of damage after only 3–4 h at 50°C above their upper temperature limit, whereas dimethylpolysiloxane will exhibit no overt signs of damage under analogous conditions.

If a column is overheated in the presence of oxygen, rapid and extensive stationary phase degradation occurs. A leak in a gas line, injector, or any area within the flow path of the carrier gas can introduce a large amount of air (and therefore oxygen) into the column. Small leaks, especially in the more obscure or unusual locations, can go undetected for long periods of time. The small amount of air that is introduced into the carrier gas is enough to damage the column over a period of a few weeks. Large leaks can introduce enough air to produce damage after 1 day. Even at temperatures well below the column's upper temperature limit, oxygen causes substantial damage to the stationary phase at a surprisingly fast rate. Prolonged exposure of a column to oxygen at high temperature is the most common source of premature high column bleed. The exposure of columns to oxygen at room temperature is not a problem; usually temperatures above 50°C are necessary for damage to occur. The exposure of columns to oxygen for a very short duration, such as when changing septa, does not introduce enough air for significant column damage to occur. It is constant oxygen exposure over a longer period of time that causes the most damage.

Repeated injections of samples containing mineral acids and bases (e.g., sulfuric acid, sodium hydroxide, etc.) may damage the stationary phase. One of the symptoms is excessively high column bleed. In most of these cases, cutting 1–2 m from the front of the column restores column performance. If a column has been thermally damaged (with or without oxygen exposure), the entire length of column is damaged; thus, cutting the column will not restore its performance. If the injected samples do not contain any potential damaging species, a thorough leak check of the entire GC system is warranted. A leak is the most probable cause of the short column life in this specific case.

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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Associate Editor