

Gas Chromatography Problem Solving and Troubleshooting

Question:

I have experienced rapid capillary column damage with less than 50 injections of a soil sample. The samples were thoroughly extracted and neutralized to pH 7 using NaOH. I have obtained substantially longer column lifetimes with other pH 7 samples. What is the cause of the short column lifetimes with this particular set of soil samples?

Answer:

There may be several factors to consider in this case. Inorganic acids such as hydrochloric, sulfuric, phosphoric, nitric, and chromic acids and inorganic bases such as potassium and sodium hydroxide can rapidly damage capillary columns. The stationary phase polymer and fused-silica tubing surface is damaged or altered by these compounds. Regardless of the sample pH, the presence of inorganic acids and bases in the injected sample usually leads to column degradation. Even if the sample is buffered or neutralized, acid and base species are introduced into the column after sample vaporization in the injector. Injection techniques such as splitless and on-column injection usually result in faster column degradation. These techniques focus or concentrate large amounts of the sample at the front of the column. Most inorganic acids and bases do not readily elute from capillary columns; thus, they accumulate in one area and severely damage the column. Most of the damage is localized to the first meter of the column. Trimming off the first meter of the column removes the contaminated or damaged portion, and column performance is often returned. Depending on the concentration of the acid and/or base, trimming the column may not reverse the performance loss. Obviously, higher concentrations of an acid or base result in faster and more extensive column damage. By adding sodium hydroxide to the soil sample extract, the injected sample becomes the cause of the short column lifetime. Depending on the ionic species present in the extracted sample, it may have been better to leave the extract at its original, lower pH. If an inorganic acid was responsible for the low sample pH, column damage would still result. Adding sodium hydroxide would only make the problem worse. For any type of sample, the ionic species in the sample is often more important than the sample pH.

In addition to the damage caused by the presence of an acid or base, the formation of nonvolatile salts may have also contributed to the short column life. For example, adding sodium hydroxide to a sample containing sulfuric acid results in the formation of sodium sulfate or a similar species. Upon injection of the sample, some of the sodium sulfate (along with some sulfuric acid and sodium hydroxide) is introduced into the column. Because it is nonvolatile, the sodium sulfate remains at the front of the column. Subsequent injections add to the accumulated material, with eventual contamination of the column. This contamination degrades column performance, and the resulting poor peak shapes are often mistakenly attributed to column damage. Much like acid- or base-induced column damage, trimming the front of the column often returns column performance. In a severe contamination problem, rinsing the column with water may be the only solution. The column manufacturer should be consulted to determine whether the column can be safely rinsed with water.

If a sample needs to be at a specific pH, whenever possible, use a volatile organic acid or base to adjust the pH. Acetic acid or trimethylamine are often used for this purpose. If an inorganic or very strong acid or base is needed, hydrochloric acid or ammonium hydroxide are the least damaging, depending on the amount of water retention of the column. If water is not retained by the column, the hydrochloric acid or ammonia rapidly travels through the column, and little or no damage occurs. If water is retained, the amount of damage is related to the degree of water retention. If the water is strongly retained, the hydrochloric acid or ammonia remains in the column for the same amount of time as the water. This may be long enough to allow the acid or base to damage the column after numerous injections.

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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