What are the major Causes of GC Capillary Column Performance Degradation?

Major Causes of Column Performance Degradation

Column Breakage

Fused silica columns break wherever there is a weak point in the polymide coating.The polymide coating protects the fragile but flexible fused silica tubing. The continuous heating and cooling of the oven, vibrations caused by the oven fan, and being wound on a circular cage all place stress on the tubing. Eventually breakage occurs at a weak point. Weak spots are created where the polymide coating is scratched or abraded. This usually occurs when a sharp point or edge is dragged over the tubing. Column hangers and tags, metal edges in the GC oven, column cutters, and miscellaneous items on the lab bench are just some of the common sources of sharp edges or points.

It is rare for a column to spontaneously break. Column manufacturing practices tend to expose any weak tubing and eliminate it from use in finished columns. Larger diameter columns are more prone to breakage. This means that greater care and prevention against breakage must be taken with 0.45-0.53 mm I.D. tubing than with 0.18-0.32 mm I.D. tubing.

A broken column is not always fatal. If a broken column was maintained at a high temperature either continuously or with multiple temperature program runs, damage to the column is very likely. The back half of the broken column has been exposed to oxygen at elevated temperatures which rapidly damages the stationary phase. The front half is fine since carrier gas flowed through this length of column. If a broken column has not been heated or only exposed to high temperatures or oxygen for a very short time, the back half has probably not suffered any significant damage.

A union can be installed to repair a broken column. Any suitable union will work to rejoin the column. Problems with dead volume (peak tailing) may occur with improperly installed unions.

Thermal Damage

Exceeding a column's upper temperature limit results in accelerated degradation of the stationary phase and tubing surface. This results in the premature onset of excessive column bleed, peak tailing for active compounds and/or loss of efficiency (resolution). Fortunately, thermal damage is a slower process, thus prolonged times above the temperature limit are required before significant damage occurs. Thermal damage is greatly accelerated in the presence of oxygen. Overheating a column with a leak or high oxygen levels in the carrier gas results in rapid and permanent column damage. Setting the GC's maximum oven temperature at or only a few degrees above the column's temperature limit is the best method to prevent thermal damage. This prevents the accidental overheating of the column. If a column is thermally damaged, it may still be functional. Remove the column from the detector. Heat the column for 8-16 hours at its isothermal temperature limit. Remove 10-15 cm from the detector end of the column. Reinstall the column and condition as usual. The column usually does not return to its original performance; however, it is often still functional. The life of the column will be reduced after thermal damage.

Oxygen Damage

Oxygen is an enemy to most capillary GC columns. While no column damage occurs at or near ambient temperatures, severe damage occurs as the column temperature increases.In general, the temperature and oxygen concentration at which significant damage occurs is lower for polar stationary phases. It is constant exposure to oxygen that is the problem. Momentary exposure such as an injection of air or a very short duration septum nut removal is not a problem.

A leak in the carrier gas flow path (e.g., gas lines, fittings, injector) is the most common source of oxygen exposure. As the column is heated, very rapid degradation of the stationary phase occurs. This results in the premature onset of excessive column bleed, peak tailing for active compounds and/or loss of efficiency (resolution). These are the same symptoms as for thermal damage. Unfortunately, by the time oxygen damage is discovered, significant column damage has already occurred. In less severe cases, the column may still be functional but at a reduced performance level. In more severe cases, the column is irreversibly damaged.

Maintaining an oxygen and leak free system is the best prevention against oxygen damage. Good GC system maintenance includes periodic leak checks of the gas lines and regulators, regular septa changes, using high quality carrier gases, installing and changing oxygen traps, and changing gas cylinders before they are completely empty.

Chemical Damage

There are relatively few compounds that damage stationary phases. Introducing nonvolatile compounds (e.g., salts) in a column often degrades performance, but damage to the stationary phase does not occur. These residues can often be removed and performance returned by solvent rinsing the column. Inorganic or mineral bases and acids are the primary compounds to avoid introducing into a column. The acids include hydrochloric (HCl), sulfuric (H2S04), nitric (HNO3), phosphoric (H3PO4), and chromic (CrO3). The bases include potassium hydroxide (KOH), sodium hydroxide (NaOH), and ammonium hydroxide (NH4OH). Most of these acids and bases are not very volatile and accumulate at the front of the column. If allowed to remain, the acids or bases damage the stationary phase. This results in the premature onset of excessive column bleed,peak tailing for active compounds and/or loss of efficiency (resolution). The symptoms are very similar to thermal and oxygen damage. Hydrochloric acid and ammonium hydroxide are the least harmful of the group. Both tend to follow any water that is present in the sample. If the water is not or only poorly retained by the column, the residence time of the HCl and NH4OH in the column is short. This tends to eliminate or minimize any damage by these compounds. Thus, if HCl or NH4OH are present in a sample, using conditions or a column with no water retention will render these compounds relatively harmless to the column.

The only organic compounds that have been reported to damage stationary phases are perfluoroacids. Examples include trifluoroacetic, pentafluoropropanoic, and heptafluorobutyric acid. They need to be present at high levels (e.g., 1% or higher). Most of the problems are experienced with splitless or Megabore direct injections where large volumes of the sample are deposited at the front of the column. Since chemical damage is usually limited to the front of the column, trimming or cutting 0.5-1 meter from the front of the column often eliminates any chromatographic problems. In more severe cases, five or more meters may need to be removed. The use of a guard column or retention gap will minimize the amount of column damage; however, frequent trimming of the guard column may be necessary. The acid or base often damages the surface of the deactivated fused silica tubing which leads to peak shape problems for active compounds.

Column Contamination

Column contamination is one of the most common problems encountered in capillary GC. Unfortunately, it mimics a very wide variety of problems and is often misdiagnosed as another problem. A contaminated column is usually not damaged, but it may be rendered useless.

There are two basic types of contaminants: nonvolatile and semivolatile. Nonvolatile contaminants or residues do not elute and accumulate in the column. The column becomes coated with these residues which interfere with the proper partitioning of solutes in and out of the stationary phase. Also, the residues may interact with active solutes resulting in peak adsorption problems (evident as peak tailing or loss of peak size). Active solutes are those containing a hydroxyl (-OH) or

amine (-NH) group, and some thiols (-SH) and aldehydes. Semivolatile contaminants or residues accumulate in the column, but eventually elute. Hours to days may elapse before they completely leave the column. Like nonvolatile residues, they may cause peak shape and size problems, and, in addition, are usually responsible for many baseline problems (instability, wander, drift, ghost peaks, etc.).

Contaminants originate from a number of sources, with injected samples being the most common. Extracted samples are among the worst types. Biological fluids and tissues, soils, waste and ground water, and similar types of matrices contain high amounts of semivolatile and nonvolatile materials. Even with careful and thorough extraction procedures, small amounts of these materials are present in the injected sample. Several to hundreds of injections may be necessary before the accumulated residues cause problems. Injection techniques such as on-column, splitless, and Megabore direct place a large amount of sample into the column, thus column contamination is more common with these injection techniques.

Occasionally, contaminants originate from materials in gas lines and traps, ferrule and septa particles, or anything coming in contact with the sample (vials, solvents, syringes, pipettes, etc.). These types of contaminants are probably responsible when a contamination problem suddenly develops and similar samples in previous months or years did not cause any problems.

Minimizing the amount of semivolatile and nonvolatile sample residues is the best method to reduce contamination problems. Unfortunately, the presence and identity of potential contaminants are often unknown. Rigorous and thorough sample cleanup is the best protection against contamination problems. The use of a guard column or retention gap often reduces the severity or delays the onset of column contamination induced problems. If a column becomes contaminated, it is best to solvent rinse the column to removethe contaminants.

Maintaining a contaminated column at high temperatures for long periods of time (often called baking-out a column) is not recommended. Baking-out a column may convert some of the contaminating residues into insoluble materials that cannot be solvent rinsed from the column. If this occurs, the column cannot be salvaged in most cases. Sometimes the column can be cut in half and the back half may still be useable. Baking-out a column should be limited to 1-2 hours at the isothermal temperature limit of the column.

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