GC Troubleshooting

Courtesy of OV Scientific

The gas chromatograph and capillary column function as a complete system and not as two individual parts. A problem or deficiency in any part of the system usually will result in some type of chromatographic difficulty. The same problem can be caused by a number of different system deficiencies. A logical and controlled troubleshooting procedure will quickly and accurately identify the source of the problem. This will result in the fastest, easiest and most complete solution to the problem.

Troubleshooting is a skill that becomes easier with practice. Someone equipped with the right tools and a rudimentary understanding of capillary column gas chromatography, can identify, locate and correct problems with minimal amount of effort.

Troubleshooting Tools

Flowmeter
A digital or manual model with a range of 10 to 500 mL/min is suitable.

New Syringe
A working syringe that has not been used for samples should be available. Some problems may actually be syringe or autosampler related.

Methane or Another Nonretained Compound
A non-retained compound is used to set and verify carrier gas flow and to check out injector operation and setup.

New Septa, Ferrules and Injector Liners
These are used to replace parts that eventually become defective, worn out or dirty.

Leak Detector
Electronic models are recommended. Liquid leak detection fluids are satisfactory ,but care has to be exercised to avoid possible contamination problems.

Column Test Mixture or Reference Sample
These are used to diagnose select system and column problems. They are useful to compare current system performance to past performance.

Checkout Column
This is a column that is not used for samples. The performance and quality is known so that evaluation of the system can be made. It helps to verify or eliminate the previous column as the source of a problem.

Instrument Manuals
These are not a last resort. The manuals are a good source of troubleshooting information special to a particular model of gas chromatograph. Performance specifications are often contained in the manuals.

Eight Problem Categories

Most performance problems can be placed within one of eight areas. These are baseline disturbances, irregular peak shapes or sizes, retention time shifts, loss of separation or resolution, quantitation difficulties, rapid column deterioration, ghost peaks and broad solvent fronts. It is not uncommon to have more than one of these problems occurring at the same time. Sometimes, it is difficult to determine the actual nature of the problem. This makes a logical and systematic approach to problem solving very important.

It is important to realize that the following comments and recommendations are generalizations and simplifications. Every possible problem or correction cannot be covered, nor can every detail be mentioned. For more information, call OV.

Baseline Disturbances

Spiking:

1. Particulate matter passing through the detector.
   Solution: Clean the detector per the instruction manual.
2. Loose connections on cables or circuit boards (usually random spiking).
   Solution: Clean and repair the electrical connections as needed.

Noise:

1. Contaminated injector and/or column.
   Solution: Clean the injector. Solvent rinse the column.
2. The column is inserted into the flame of an FID, NPD or FPD.
   Solution: Reinstall the column.
3. Air leak when using an ECD or TCD.
   Solution: Find and repair the leak.
4. Incorrect combustion gases or flow rates when using an FID, NPD or FPD.
   Solution: Check and reset the gases at their proper values.
5. Physical defect in the detector.
   Solution: Clean or replace parts as necessary.
6. Defective detector board.
   Solution: Consult the instruction manual or contact the GC manufacturer.

Wander:

1. Contaminated carrier gas if using isothermal conditions.
   Solution: Change the carrier gas or use (change) carrier gas impurity traps.
2. Contaminated gas chromatograph.
   Solution: Clean the injector and/or gas lines. Solvent rinse the column.
3. Poor control of the carrier gas or detector gas flows.
   Solution: Clean, repair or change the flow controller.
4. Poor thermal control of the detector.
   Solution: Consult the instruction manual or contact the GC manufacturer.

Drift (Upward):

1. GC or column contamination.
   Solution: Clean the injector. Solvent rinse the column.
2. Damaged stationary phase.
   Solution: Replace the column. Determine the cause of the damage (oxygen, thermal or chemical) to prevent future problems.

Drift (Downward):

1. Incomplete conditioning of the column.
   Solution: Condition the column until a stable baseline is obtained.
2. Unequilibrated detector.
   Solution: Allow the detector enough time to equilibrate.

Offset:

1. Injector or column contamination.
   Solution: Clean the injector. Solvent rinse the column.
2. Column is inserted into the flame of an FID, NPD or FPD.
   Solution: Reinstall the column.
3. Contaminated carrier or detector gases.
   Solution: Change the gases or install (change) impurity traps.
4. Contaminated detector.
   Solution: Clean the detector.
5. Malfunctioning or improperly set recording device.
   Solution: Check the recorder settings. Consult the instruction manual, or contact the manufacturer.

Irregular Peak Shapes or Sizes

No Peaks:

1. Plugged syringe.
   Solution: Clean the syringe or use a new syringe.
2. Broken column.
   Solution: Replace or reinstall the column.
3. Injecting the sample into the wrong injector.
   Solution: Use the correct injector or move the column to the correct injector.
4. Column installed into the wrong detector.
   Solution: Reinstall the column into the correct detector.
5. Integrator or recording device is connected to the wrong detector or not connected at all.
   Solution: Connect the integrator to the correct detector.
6. Detector gases improperly set or not on.
   Solution: Check and reset the detector gases.
7. Very low or no carrier gas flow.
   Solution: Immediately lower the column temperature to 35-40°C. Measure and verify the carrier gas flow rate. Check for leaks.

All Peaks Reduced in Size:

1. Partially plugged syringe.
   Solution: Clean the syringe or use a new syringe.
2. Change in the injection technique.
   Solution: Check the injection technique and verify that it is the same as before.
3. Large leak in the injector (usually accompanied by poor peak shapes).
   Solution: Find and repair the leak.
4. Split ratio is too high.
   Solution: Lower the split ratio.
5. Too short of a purge activation time for split less injections.
   Solution: Increase the purge activation time.
6. Very high septum purge flow.
   Solution: Decrease the septum purge flow.
7. Too low of an injector temperature (especially for high molecular weight or low volatility compounds).
   Solution: Increase the injector temperature .
8. Column temperature is not hot enough.
   Solution: Increase the column temperature or the upper temperature value of the column temperature program.
9. Initial temperature of the column is too high for split less or on-column injections.
   Solution: Decrease the initial column temperature or use a higher boiling solvent.
10. High background signal caused by contamination, excessive column bleed (damage) or auto zero problem.
    Solution: Clean the GC. Solvent rinse the column. Replace the bleeding column. Check the auto zero function and setting.
11. Improperly operated detectors.
    Solution: Consult the instruction manual for the proper gas flows and type and operating guidelines.
12. Impurities in the detector gas.
    Solution: Use impurity traps and/or replace the contaminated gas.
13. Detector-compound mismatch.
    Solution: Make sure that the detector will respond to the compounds being analyzed.
14. Excessive attenuated integrator signal.
    Solution: Check and verify the attenuation settings.
15. Sample concentration or integrity problems.
    Solution: Check the sample's concentration or stability.

Select Peaks Reduced in Size:

1. Column and/or liner activity or contamination, if the reduction or loss is for active compounds (e.g., amines, carboxylic acids, alcohols, diols).
   Solution: Clean or replace the injector liner. Solvent rinse or replace the column.
2. Leak in the injector, if the reduction or loss is the most volatile compounds.
   Solution: Find and repair the leak.
3. Too high of an initial column temperature for split less or on-column injections.
   Solution: Decrease the initial column temperature or use a higher boiling solvent.
4. Mixed sample solvents for split less or on-column injections.
   Solution: Use a single solvent for sample injection.

5. Decomposition or error in the sample.
   Solution: Check and verify the sample integrity and concentration.

Tailing Peaks:

1. Active injector liner or column.
   Solution: Clean or replace liner. Replace the column if it is damaged.
2. Contaminated injector liner or column.
   Solution: Clean or replace the injector liner. Solvent rinse the column.
3. Dead volume caused by a poorly installed column, liner or union.
   Solution: Check and verify the installation of each fitting. Re-install the column, if necessary.
4. Poorly cut column end.
   Solution: Recut and reinstall the column.
5. Polarity mismatch of the stationary phase, solute or solvent.
   Solution: Change to a solvent or phase that have a better polarity match.
6. Cold spot in the flow path.
   Solution: Check the flow path of the sample for possible cold spots or zones.
7. Solid debris in the liner or column.
   Solution: Clean or replace the liner. Cut the ends of the column until the debris is removed.
8. Poor injection technique (usually too slow of an injection).
   Solution: Change injection technique.
9. Too low of a split ratio.
   Solution: Increase the split ratio.
10. Overloading on a PLOT column.
    Solution: Decrease the amount of sample reaching the column.
11. Some compounds such as alcoholic amines, primary and secondary amines, and carboxylic acids tail on most columns.
    Solution: Use a pH-modified stationary phase. Derivative the compounds. Some peaks will always exhibit some tailing.

Rounded or Flat-Topped Peaks:

1. Overloaded detector.
   Solution: Decrease the amount of sample reaching the detector.
2. Exceeding the range of the integrator or recording device (especially for computer systems).
   Solution: Reset the range or attenuation levels on the recorder.

Split Peaks:

1. Poor injection technique (jerky or erratic).
   Solution: Change injection technique (smooth and steady plunger depression).
2. Poorly installed column in the injector.
   Solution: Recut the column end and reinstall in the injector.
3. Column temperature fluctuations.
   Solution: Check the oven temperature or contact the GC manufacturer.
4. Coelution of two or more compounds.
   Solution: Check for any changes in the operational parameters. Contamination or a change

in the sample will introduce additional compounds to the injected sample. Check for these possibilities.
5. Mixed sample solvent for split less or on-column injections.
   Solution: Use a single solvent for sample injections.

Negative Peaks:

1. All peaks are negative.
   Solution: Check the polarity of the recorder connections.
2. Select peaks on a TCD.
   Solution: Compound has greater thermal conductivity than the carrier gas; a negative peak is expected in this case.
3. After a positive peak on an ECD.
   Solution: Dirty or old ECD cell. Clean or replace the ECD.

Retention Time Shifts

1. Different column temperature.
   Solution: Check and verify the column temperature or temperature program.
2. Different carrier gas flow rate or linear velocity.
   Solution: Check and verify the carrier gas flow rate or linear velocity.
3. Leak in the injector, especially the septum.
   Solution: Find and repair the leak. Change the septum.
4. Contaminated column.
   Solution: Solvent rinse the column.
5. Change in the sample solvent.
   Solution: Use the same solvent for all samples and standards.

Loss of Separation or Resolution

1. Contaminated column.
   Solution: Solvent rinse the column.
2. Damaged stationary phase.
   Solution: Replace the column. Excessive bleed should be evident also.
3. Different column temperature, carrier flow rate or column.
   Solution: Check and verify temperature programs, flow rates and column identity.
4. Large changes in the sample concentration.
   Solution: Adjust or compensate for the concentration change.
5. Improper injector operation.
   Solution: Check the temperature, split ratio, purge time and type of liner. Also check for leaks.

1. Quantization Difficulties

2. Injection technique.
   Solution: Use a consistent injection technique.
3. Split discrimination.
   Solution: Use a consistent injection technique (volume, injector temperature and split ratio).
4. Using a different purge activation time for split less injection.

Solution: Use a consistent purge activation time.

5. Baseline disturbances.
   Solution: See the section on baseline disturbances
6. Improper integrator or recorder settings.
   Solution: Check and verify the integrator and recorder settings.
7. Inconsistent detector gas flows or temperatures.
   Solution: Check and verify detector operation.
8. Column or liner activity (adsorption).
   Solution: Clean or replace the injector liner. Solvent rinse or replace the column.

Rapid Column Deterioration

1. Exposure of the column to air (oxygen) at elevated temperatures.
   Solution: Find and repair any leaks. Check the quality of the impurity traps and carrier gas.
2. Exceeding the upper temperature limit of the column for prolonged periods.
   Solution: Replace the column. Do not exceed the upper temperature limits.
3. Chemical damage.
   Solution: Do not inject inorganic acids or bases.
4. Contamination of the column with high molecular weight mate rials.
   Solution: Use a sample preparation technique to remove the problem contaminants. Use a guard column.
5. Column breakage.
   Solution: Avoid abrading or scratching the column. Avoid sharp turns or bends in the tubing.

Ghost Peaks

1. Contamination of the injector or column.
   Solution: Clean the injector and liner. Solvent rinse the column.
2. Septum bleed.
   Solution: Use a higher temperature septum. Lower the injector temperature. Condition septum before use.
3. Previous run terminated too soon.
   Solution: Use a higher temperature to elute all of the sample components. Prolong the run time to allow the complete elution of the sample.

Broad Solvent Front

1. Poorly installed column.
   Solution: Recut and reinstall the column.
2. Leak in the injector.
   Solution: Find and repair the leak.
3. Too low of a split ratio.
   Solution: Use a higher split ratio.
4. Too low of an injector temperature.
   Solution: Use a higher injector temperature.

5. Too long of a purge activation time for split less injections.
   Solution: Use a shorter purge activation time.
6. Large injection volume.
   Solution: Decrease the injection size.
7. Low column temperatures and high boiling solvent.
   Solution: Use a higher initial column temperature or a lower boiling solvent.
8. High column temperatures and low boiling solvent.
   Solution: Use a lower initial
   column temperature or a higher boiling solvent.

OV F51 Model Flowmeter
Flow rates are critical to efficient GC operation. Make sure flow rates are correct by using the OV F51 Model series of flowmeters. They are based on "acoustic displacement" technology. No bubbles, messy liquids or breaking glassware to deal with. Ideal for field or laboratory use. These flowmeters are compatible with all noncorrosive gases. A computer-optimized calibration incorporating a NIST calibrated flow standard ensures the highest available accuracy, making ISO9000 and GLP compliance that much easier.

Hamilton Cemented Needle
Be sure to have a clean, working syringe. Problems can sometimes be traced to the autosamplers. Chrom Tech offers a complete line of Hamilton Syringes.

Septa and Ferrules
J&W offers a complete line of silicone septa and ferrules. Overused septa and ferrules are prone to leaks, which can cause column bleed due by allowing oxygen to be introduced. Particulates from the overused septa and ferrules can also cause problems when they contaminate the liner.

4 mm Split less Liner
Pyrolyzed compounds can build up on liner walls. This buildup causes clogging and sample adsorption, which can result in a non representative chromatogram.

TROUBLESHOOTING: GC: "Low-Bleed" columns -- fact or fiction?

Several manufacturers offer "low bleed" columns. In some cases, these are merely selected from the standard production process, but in other cases the columns are actually "synthesized" for low bleed. In recent years, it has been established that where functional groups (i.e. phenyl) are inserted into the polysiloxane chain as aryl inclusions, as opposed to being attached to the chain as pendant groups, the resultant phase possesses increased thermal and oxidative resistance. Columns coated with such phases emit lower levels of bleed signal and are capable of going to higher temperatures. The increased thermal resistance is apparent only at temperatures above ca. 300 degrees. While some users can reap the benefits of these developments, others find little or no improvement.. their bleed signals are still too high.

True column bleed, of course, comes only from the column. What the user perceives as bleed is usually the total signal reaching the detector, which is the summation of signal from the septum (this gives a typical silicone mass spectrum), the injector, and the

detector, all of which is usually blamed on the column.

It is good procedure to first check the detector. Disconnect and remove the column, and place an undrilled cap on the column attachment fitting. Activate the detector, and note the signal at 50 degrees. Increase the oven temperature to 320 degrees, and again note the signal. On a pristine detector, the FID signal will increase by one to two picoamps. If the increase exceeds this level, attention should be directed to cleaning the detector, make-up gas and hydrogen lines. Once the detector signal falls to an acceptable level at 320 degrees, attention should be directed to the injector. If the injector liner is visibly soiled, the injector should be cooled, dissembled and interior cavities scrubbed with solvent and natural bristle brushes or cotton swabs. After assembling the injector, a "jumper tube" (one to three meters of uncoated fused silica or steel tubing) is then used to connect the injector directly to the detector. The injector heater should be energized, and the oven set at 320 degrees. Any increase in "bleed" signal over that observed with the detector alone must come from the front end of the instrument, and may originate with the septum, the carrier gas line, in-line regulators, valves, or flow controllers.

Wrap a new septum in aluminum foil, ensuring that one face is smooth, and install this, smooth side down. If the signal emanating from the jumper tube is decreased, it indicates a need for better quality septa. If the signal is still high, materials entrained in the carrier gas may have deposited in lines, valves, or regulators, which should be dissembled and cleaned or replaced.

When the combined signal from the injector and detector falls to an acceptable level (one to two picoamps @ 320 degrees on an FID), the user is ready to install and reap the benefits of a true low-bleed column. The bleed rate of conventional columns is normally high enough to mask signal from the injector and detector unless these latter are heavily contaminated. With low bleed columns, the signal from the injector and detector assumes increased importance. This spurious signal is not infrequently limiting, and is usually (and incorrectly) perceived as "column bleed".

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A Message from Walt: Column Activity

The requirements for qualitative and quantitative validity that confront today's analysts demand the ultimate in analytical GC columns. Column quality is reflected not only by column efficiency (usually measured in N/m), by the "delta bleed" (signal at max temp versus signal at 50°), by the maximum usable temperature, and by the duplicability of the "selectivity" (usually measured via the retention indices of selected compounds), but also by the level of "column activity". Some of these are inter-related.
Activity exercises negative effects on both qualitative and quantitative analyses. Properly used, octanol and decanol are useful analytes to follow column activity, but it is possible to manipulate their behavior. Alcohols tail because they undergo hydrogen bonding with active sites on the column (or the stationary phase), and the strength of hydrogen bonds varies inversely with temperature. Columns that exhibit unacceptable tailing at test temperatures of 100-125° often generate needle sharp alcohol peaks at 150-180°, and while this generates an impressive test chromatogram, it is unrealistic because these

solutes elute at much lower temperatures -- where H-bonding is stronger -- in a real run.

The increased emphasis on low bleed columns has made many analysts more aware of this problem. One method of producing a "low bleed" column is lengthy exposure to excessive temperatures. Unfortunately, this usually results in a very active column, but the reasons for this are not entirely clear. We recognize that deactivation treatments are often more thermally labile than is the stationary phase per se, but whether the end result is due to the exposure of active silanols or to some other source of activity remains to be elucidated.

There is much to be said for the common polarity test mixture -- usually containing paraffin hydrocarbons, esters, ketone(s), primary alcohols, and one or two more demanding analytes -- e.g., diols, primary amines, and/or halogenated phenols. The discriminating analyst sometimes adds a specific test compound(s) that reflects his or her particular requirements. If there is any possibility that any of the analytes in the test mixture could interact with each other on long term storage, some precautions are in order. Two or more solutions should be prepared, each containing only analytes immune to interaction, and aliquots of these inert solutions blended to produce the intact test solution just prior to analysis.

The hydrocarbons are crucial to the test mixture; they serve as reference peaks. Paraffin hydrocarbons have no active entities, and tailing of a hydrocarbon peak is almost always indicative of a gas flow problem (too low a split ratio, inadequate make-up gas, cracked injector liner, etc.). Only if (or when!) the hydrocarbon peaks are sharp and symmetrical can the conformation of the peaks produced by the more active analytes be realistically evaluated. Columns that have been subjected to analysis of dirty samples and/or exposure to excessively high temperatures for sustained periods should be periodically re-tested. Unfortunately, it is rarely possible to re-deactivate heat-damaged columns without adversely affecting some of their other properties. In the next "Message", we'll examine some means of prolonging column life.

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