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Diagnosing and Resolving GC Problems

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DIAGNOSING AND RESOLVING GC PROBLEMS

For all discussions, we will assume you are running Volatiles by GC/MS (524, 624, 8260) and/or Semivolatiles by GC/MS (525, 625, 8270). Other non-Mass Spec applications are not addressed here. Since it is rare for these units to “break”, the majority of problems with them ends up being with conditions being set incorrectly or for the system to develop leaks and/or active sites.

Detecting and Resolving Leaks:

Here are some good ideas to follow in order to detect and fix leaks:

- The MSD can detect leaks where air is being sucked into the ion source (by virtue of the presence of large amounts of ions 28 and 32), but it has no ability whatsoever to detect leaks where Helium and analytes are being lost OUT of the system. To detect these leaks you need to monitor flows and/or use a leak detector.
- Once per month, when the system is running optimally, measure the split vent flow and record it in a log book. Monitoring changes in split vent flow is the best way to detect leaks. This applies to 5890 GCs. 6890 GCs will automatically add more flow if a leak exists, so in this case if you notice reduced areas of your analytes, you will need to check the inlet with a Helium leak detector.
- Whenever you dismantle the injector to do maintenance, ALWAYS measure the split vent flow immediately before and immediately afterwards. If you have done it correctly, they will be identical. If not, you need to check everything you did prior to heating up the inlet and running the system. As above, this applies to 5890 GCs. For 6890 GCs you will need to check the inlet with a Helium leak detector.
- Monitor the areas of your first Internal Standard. If the areas drop off, yet the sensitivity of the MSD (as measured by the raw abundance of ion 69 in Manual Tune) is constant, check for leaks. For Semivolatile analysis the leak is likely to be in the inlet. For Volatiles, it's more likely to be in the purge and trap than the GC so you should leak check the purge and trap.

- It's a very good idea to purchase a hand-held Helium leak detector. It's a lot to spend I know but it's an invaluable tool when trying to find small leaks.
- Never try to detect leaks by squirting a fitting with soapy water to see if it bubbles. You can get some of the soap into the lines and that would be disastrous.

If a leak does occur in your inlet, check the following:

- Carefully inspect the glass liner. If it is chipped, that would cause a leak.
- Check the Viton O-ring that seals the liner. It should feel elastic. If in doubt, change it.
- Replace the septum if it has been punctured many times or has been crushed out of shape. Be careful not to over tighten the septum nut as that can cause the septum to become crushed. 1/4 turn past finger tight should do it on the septum nut.
- Replace the inlet seal if the face seems worn out or warped. This sometimes happens if it has been used and reused a lot or has had the face cleaned to remove debris.
- Re-seal the fitting from the column to the inlet. Be careful not to over tighten the fitting, as this can cause the ferrule to get cracked.

Coping with Active Sites

Another common problem with inlets is the development of active sites. An active site is any buildup of contamination that would cause a compound to react with or adsorb to, thereby compromising the integrity of the analysis.

For Volatiles, active sites in the inlet generally only occur if a sample foams over. Otherwise, you would typically only do your injector maintenance once a year on average.

For Semivolatile analysis, fighting active sites is nearly an every day battle because of the beating the inlet takes by having numerous Methylene Chloride extracts injected into it. Active sites in the inlet can cause many compounds (especially Benzidine and the Phenolics) to show drastically reduced response.

Here are some ways to minimize and/or cope with active sites for Semivolatiles:

- Use common sense before injecting a dirty looking extract. If an extract is very brown, or very viscous, or came from a sample you know is loaded, dilute the extract 1:10 and then run it. Based on this run you can determine if it's safe to run a full strength. It's a good rule of thumb to "dilute the extract first, ask questions later".
- Having an inert inlet sleeve is essential. Unless you are running VERY clean samples, you would probably benefit from using silanized fused silica wool/inlet sleeve combination.
- Buying silanized liners is a very costly procedure. I suggest you follow the procedure listed below and do it yourself. All you need to do is buy a 5-pack of 4 mm single gooseneck liners and a tin of untreated fused silica wool. Then, make 4 solutions in 4 vials as listed below and do it yourself. It's a very simple and inexpensive way to always have deactivated liners and plugs on-hand. You can re-use the liners; simply remove the plugs each day (or as needed after running a batch of dirty extracts), rinse with Methanol, dry them, insert a new plug and repeat the entire silanizing process. If you want an explanation as to the chemistry involved in the deactivation, simply e-mail me and I'll send it to you.

Procedure to Silanize Injection Port Liners for Semivolatiles

Step 1: You need to prepare 4 vials (40 mL VOA vials are ideal) as follows:

Vial 1: 10% DCDMS (Dichlorodimethyl Silane) in Toluene. 36 mLs Toluene + 4 mLs DCDMS. You can get DCDMS from Sigma-Aldrich. The percentage need not be exact.

Vial 2: Toluene (as a rinse)

Vial 3: Initial Methanol

Vial 4: Final Methanol

Step 2: You need to place a fused silica wool plug in the liner BEFORE silanizing. Use a 4 mm ID liner with a small, loosely packed fused silica wool plug about 1/4" long

Steps 3-7: Simply soak the liner with plug in each vial for two hours or so-from Vial 1 to Vial 4 (if time permits allow them to soak overnight). After the 4th vial, dry the liner in a drying oven (120 °C) and keep the dried liners air-tight. Be careful not to chip the glass liners when handling them as the slightest chip will cause a leak when inserted into the injection port.

After running "dirty extracts", cool the injection port, remove the plug, rinse the liner (do not use detergents) and repeat the process. Note: HCl gas is given off as a by-product of the reactions so handle the vials with care and store them in a fume hood:

- Clip off 1/5 meter of column (8 inches) daily or when needed. If peak shape or responses are poor, clip off 2 loops.
- Change autosampler rinse solvents daily. It's Ok to use Methanol if the BNA GC/MS is in the same room with the VOA GC/MS. If not, use Methylene Chloride as rinse solvent #1 and Acetone as rinse solvent #2.
- Avoid injecting more than 1.0 uL into H-P split/splitless injectors. Injecting 2.0 uL generally only increases areas by about 30% but peak shape suffers from overloading the liner. If you have a 5 uL syringe you can inject 0.5 or 1.5 uL, so this may be a good solution if you're having sensitivity problems.

GC Problem: Injector pneumatics

OK, let's say you're still having GC problems even though you've installed a new column and properly done all the injector maintenance. The problem could very well be the injector pneumatics rather than the injector consumables. Injection ports pneumatics periodically need to be replaced because the lines and valves become contaminated with non-semivolatile residue.

Here are the components of the split/splitless pneumatics for the 5890 GC:

- 5890 shell weldment
- 5890 splitter tube
- 5890 split/splitless solenoid valve
- 5890 split weldment
- 5890 EPC Proportional control valve

It's a good idea to periodically clean the shell weldment. To do this, first cool the inlet. Then remove the column. Then remove the liner, O-ring and inlet disc. Then take a bristle test-tube brush and scrub the inside of the shell weldment with Acetone. This will often help remove any dried-on debris that has accumulated on the inside surface. If it still looks grimy to you after cleaning, it's worth the money to replace it.

The splitter tube and split weldment are next to impossible to clean and are inexpensive enough to justify replacement.

The EPC valve and split/splitless solenoid valve cannot be cleaned. You would suspect that the EPC valve needs replacement if the GC cannot maintain the set head pressure (this sometimes makes the system “beep”). If you don’t have a leak, then a defective EPC valve is probably the culprit with this problem.

Here are the components of the split/splitless pneumatics for the 6890 GC:

1. 6890 shell weldment
2. 6890 splitter tube (1/8” copper)
3. 6890 split gas filter
4. 6890 split weldment
5. 6890 split/splitless flow module- (integrated flow/pressure control assembly which slides in slot on top of the GC)

Part #5 above is very expensive, so try a “mini” injector rebuild by replacing parts #1-4 above. If that fails to restore performance, or if the system cannot hold head pressure, then replace part #5 as well.

Another way to know you have contaminated pneumatics is by monitoring Benzidine. If your Benzidine response is very low when you run a 50 ppm full 625/8270 standard, run the a 50 ppm Benzidines standard alone. If the area is much higher in the Benzidines standard alone, then that’s a good hint your injector pneumatics are contaminated. If you have EPC, you probably won’t need a new EPC valve as long as the system is holding head pressure.

Final note: Replacing injector pneumatics can be a costly expense, but one that’s well worth it. If you have been running your GC for methods 625/8270 for years, chances are the pneumatics are somewhat contaminated. At some point they will become so bad that the problems are insurmountable without overhauling the inlet. Installing new injector pneumatics into a GC basically gives it a “new lease on life” and should restore the GC to “like-new” condition.

GC Problem: Column and conditions

Another common GC problem would be defective column, improper installation, or non-optimized conditions. At this point I want to discuss the flows and pressures of the split/splitless injector for semivolatiles analyses.

Although the flow path with the 6890 is slightly different than the 5890, for this discussion the points I want to make apply to both.

It’s important to understand the flow path of the split/splitless injection port in order to optimize conditions and troubleshoot problems.

Let’s assume the TOTAL FLOW into the injector is 43 mL/min. We can’t measure that directly, but can easily compute it by adding the 3 flows into which the total flow splits. The flow comes into the split/splitless injection port and then is routed in 3 directions as follows:

1. About 2.0 mL/min hovers under the septum and exists via the septum purge vent. For EPC systems it is set to about 2.0 mL/min; for non-EPC systems it has to be set manually and we recommend about 2 mL/min. This flow can be measured via a flow meter.
2. About 1.0 mL/min enters the column. The exact flow is a combination of column ID, head pressure applied and temperature programming used. Typically, a 0.25 mm ID column is used with head pressures ranging from 10-25 psi, the column flow ends up being about 1.0 mL/minute on the average, so we’ll use that figure in our calculation. We can measure this flow by doing a linear velocity check, but that’s usually not necessary as we can estimate the flow to be about 1.0 mL/minute.
3. The rest of the flow, called the split vent flow, passes through the split/splitless injection solenoid and exists via the split/splitless vent. For semivolatiles we typically set it to 40 mL/min. This flow can be measured via a flow meter. Here’s where the split/splitless part comes in.
 - In the SPLIT MODE (also called the Purge “on” mode), the flow sweeps through the inlet liner sleeve, then through the split/splitless injection solenoid and then out the vent.
 - In the SPLITLESS MODE (also called the Purge “off ” mode), most of the flow bypasses the inlet liner sleeve, then passes through the split/splitless injection solenoid and then out the vent. There is enough flow through the liner to maintain head pressure.

When setting our method, we want the inlet in the SPLITLESS MODE (also called the Purge “off ” mode) at time of injection and for however long it takes for the solvent cloud to pass through the liner and enter the column. Once that happens, we cycle the split/splitless injection solenoid so as to have the inlet in the SPLIT MODE (also called the Purge “on” mode), thereby sweeping the inlet of any residual solvent, contamination, air, or other material that we DON’T want in the column.

So, by using the split/splitless injection port in the SPLITLESS mode, we essentially allow virtually all that is injected to enter the column. This helps us maximize the signal. Once the analytes are into the column, we cycle it

to SPLIT mode, which keeps the inlet clean and reduces the noise we would otherwise get. It's a simple, yet elegant and effective system for obtaining good signal-to-noise chromatograms.

So, the total flow into the injector is the sum of all 3 sub-flows, namely 2.0 mL/min (septum purge vent) + 1.0 mL/min (carrier flow) + 40 mL/min (split vent flow)= 43.0 mL/min TOTAL flow into the injector.

An important variable is Purge "On" Time. This is the time that the system stays in the Splitless (Purge "Off ") mode for at time of injection before cycling to the Split (Purge "On" Mode). Typically this is set anywhere between 0.4-1.0 mins. The way it is calculated is as follows:

- Injection volume 1.0 uL
- Liner size 2 or 4 mm ID
- Injector temperature 250 °C

A 1 uL injection of Methylene Chloride will vaporize to about 500 uL (0.5 mL) of gas upon injection in the hot inlet. If our flow is 1.0 mL/minute, then it should take 0.5 mins for that solvent cloud to pass through the liner and into the column. That is why 0.5 mins is typically used, although there's a practical range of 0.4 and 1.0 mins from which to choose. The optimum time is a function of liner size and type, head pressure at time of injection, solvent used, and injector temperature. If you're using a setting between 0.4 and 1.0 mins and achieving good results, stay with it. If not, try 0.4, 0.5, 0.75 and 1.0 mins and see what gives you the best overall results.

Troubleshooting the Split/Splitless Injector for Semivolatiles

Here are recommended inlet conditions for running Method 625/8270

Column:	30 m/0.25 mm ID/0.25 or 0.5 u Film thickness.
Injection volume:	1.0 uL
Liner size:	4 mm single gooseneck ID
Injector temperature:	250 °C (be sure to use the insulation)
Head pressure:	12 psi for Non-EPC systems, for EPC systems I like to pressure pulse or program it; 16 psi for 30 secondsvariable pressure to achieve 1.0 mL/min for balance of run for 5970 and 1.2 mL/min for 5971-5.

Assuming you have proper inlet conditions, the 2 biggest problems you will face are leaks and active sites. As mentioned earlier, leaks can often be detected by changes in split vent flow, so once per month, when the system is running optimally, measure the split vent flow and record it in a log book.

I like to monitor the response of Benzidine, 2,4-Dinitrophenol and 4-Nitroaniline to determine if active sites are present. If so, these 3 compounds are among the first to suffer. I also monitor the peak shape of 4-Nitrophenol as this is often the first compound to look "ragged" the column is in need of replacement.

Here's a good idea whenever you install a new Semivolatiles column. Before running your DFTPP and curve, it would be wise to be sure the column you just installed isn't defective and has been installed correctly.

After I install a new column, I prepare a solution of the 6 Internal Standards in Methylene Chloride at 40 ppm. You should get 6 sharp peaks with no extraneous peaks and a flat baseline throughout the run.

Here are some things to look for.

1. No ski slope early in the run. If you see a high baseline to start, then about 2 or 3 mins into the run the baseline drops back to normal, you have either an air leak or an injector problem. If you see ions 40 and 44 in the "ski" slope, you have a leaky fitting inside the GC, either at the inlet or detector. If you see ions 49,84 and 86, then you either have a clog in the column, a defective column or problems with the pneumatics. These ions would be indicative of Methylene Chloride. Presence of Methylene Chloride early in the run (i.e. eluting during or after your first target compound) means that the solvent is not being swept out of the system properly.

So if you see them during the run (which you shouldn't), the first thing to do is clip off a loop of column and re-install. If the problem persists, replace the column. If it still persists, then cleaning the split/splitless solenoid with Methanol would be indicated. If it still persists after all this then an injector rebuild would be next.
2. No rise in the baseline at the end of the run. If you see a noticeable rise in the baseline, chances are the ions would be 207 and 281. This is column bleed. Run 3 more of these test runs and see if the baseline is improving. If so, continue running these test runs until the baseline is acceptable. If the bleed doesn't dissipate, you can bake the column at 300 °C for 4 hours, but the problem with that is that any baked off bleed will contaminate

your Mass Spec. That's why thin-film, low bleed columns (0.25 µ film thickness) are desirable. A brand new column that has been conditioned overnight with these blank runs should have a good baseline the subsequent day. If not, I suggest replacing the column.

3. The height of ISTD #6 (Perylene-d12) should be at least half of that of ISTD#1 (1,4-Dichlorobenzene-d4). If you don't get the proper peak formations and/or your 6th Internal Standard is low, check the following:
 - correct injector temp (should be 250 °C)
 - be sure you have enough insulation in the lower insulation cover
 - clog in the column
 - column not inserted properly into inlet (it should be about 5 mm above the ferrule)
 - incorrect head pressure at time of injection (it should be between 10-25 psi)
 - dirty inlet disk
 - contaminated injector pneumatics
4. No stray peaks. You should see 6 sharp, crisp peaks and a flat baseline throughout. Extraneous peaks indicate either contamination in the inlet or contamination in the solvent or Internal Standard Mix.

At this point I want to discuss the flows and pressures of the split/splitless injector for Volatiles analyses.

Although the flow path with the 6890 is slightly different than the 5890, the points I want to make apply to both.

It's important to understand the flow path of the split/splitless injection port in order to optimize conditions and troubleshoot problems.

The main distinction between using the split/splitless injection port with Volatiles as opposed to Semivolatiles is that it is used only in the Split (Purge "On") mode. So, even though the term "Volatiles by split/splitless injection" is used, what's really meant is "Volatiles by split injection". This simplifies things for us.

The flow path for volatiles by split/splitless injection depends on how it was plumbed. Regardless of that aspect, the flow feeding the injection port comes from the transfer line of the purge and trap. The helium and analytes are transferred from the trap, through the 6-port valve and into the inlet during the Desorb mode.

Typically that flow is set to about 25 mL/min. Once the flow enters the injector, it is basically split 24:1, with 24 mL/min sweeping through the inlet, through the solenoid valve and out the split vent and 1 mL/min entering the column to serve as carrier flow.

For 5890 GCs, the septum vent is not needed and is either shut off or has the vent capped off. For 6890 GCs, you need to leave it in the flow path at the usual 2-3 mL/min. The head pressure used depends on whether EPC is used or not and the internal diameter of the column. Assuming you are using a 0.25 mm ID column, you can use the following as a guideline:

Systems without EPC: set the head pressure to 15 psi

Systems with EPC: set the flow to a constant flow of 1.0 mL/min or pressure pulse it so that the head pressure is high during desorb (25 psi or so) then remains constant at about 1 mL/minute thereafter.

It's a simple flow path- the flow comes in via the Purge and Trap and gets split about 24:1. You might think that this system would kill sensitivity. Indeed it does hurt sensitivity, which is why most labs tune their Mass Specs with significantly higher voltages than Semivolatiles systems. Fortunately, advances in column and electron multiplier technologies over the past few years enable labs to meet low level MDLs even with this seemingly high split ratio.

Troubleshooting the Split/Splitless Injector for Volatiles

Here are recommended inlet conditions for running Method 624/8240/524.2

- | | |
|-----------------------|--|
| Column: | 60 m/0.25 mm ID/0.25 or 1.4 µ Film thickness. |
| Liner size: | 1.0., 2.0 or even 4.0 mm ID straight (see which works best) |
| Injector temperature: | 150 °C (be sure to use the insulation). It's counterproductive to set the injector to very hot temperatures |
| Head pressure: | 15 psi for Non-EPC systems, for EPC systems I like to pressure pulse or program it; 25 psi for desorb time-variable pressure to achieve 1.0 mL/min for balance of run (1.2 mL/min for 5971-5). |

Assuming you have proper inlet conditions, the 2 biggest problems you will face are leaks and active sites. As mentioned earlier, leaks can often be detected by changes in split vent flow, so once per month, when the system is running optimally, measure the split vent flow and record it in a log book.

Active sites in the inlet can occur from buildup of acid or from “foamovers” whereby a soapy sample overflows the purge tube and some of the soapy residue actually makes it all the way to the inlet.

Periodic injector maintenance similar to semivolatiles (clipping a loop, changing the liner and disk) should be done only as needed. If no foamovers occur it's possible to go for many months without having to service the inlet.

One common problem we've seen with the Volatiles by split/splitless injection is where the Internal standard areas increase as the standard level increases.

Here's an example of what might happen. The response of your internal standard fluorobenzene (which is 5.0 ppb for all points) for your 5 point curve is as follows:

1.0 ppb= 1,656,345 counts
2.0 ppb= 1,878,620 counts
5.0 ppb= 2,014,890 counts
10.0 ppb= 2,414,450 counts
20.0 ppb= 2,868,978 counts

This inconsistency is causing your curve to be nonlinear and your surrogates to fail. What is going on here and how would you go about resolving this problem?

Answer: This is a good one. We see it happen often so we have a handle on what to do. What's happening is that the internal standard area is increasing with the concentration of your analytes. This should NOT happen. The internal standard area should be reasonably consistent in every run, be it a blank, low level standard, high level standard, or heavily loaded sample. So, what causes this?

What's happening is that the presence of other analytes is giving the “analyte slug” coming off the trap during desorb more mass and hence more inertia as it travels to the injector. The problem is either in the injection port and/or the purge and trap- possibly a leak, contamination or non-optimized conditions somewhere. The first thing to do is to leak check the system. The next thing to do would be to Methanol flush the concentrator.

If no leak or active site exists, then try changing conditions. If fluorobenzene in the 20 ppb standard shows more area than it does in the 1.0 ppb standard, then some

of the fluorobenzene may be getting lost out the split vent. Try the following to improve the consistency of the responses:

- A. Doing the injector maintenance (new liner, gold seal, septum).
- B. Adjust the desorb flow to 25-30 mL/min for 5890s, 30-35 mL/min for 6890s. Increasing the desorb flow usually mitigates this problem but hurts sensitivity so raise it as much as you can provided you can still see your low level standard.
- C. Increase the Injector temperature by 20 °C from what you have been using, then decrease it by 20 °C from what you have been using and see which direction improves results.
- D. Do the same as “C” for the heated zones in your purge and trap.
- E. If you have a fritted sparger switch to a fritless one.
- F. Clip off 2 loops of the column (replace if you suspect a sample foamover).

If all else fails, you may need an injector rebuild. Some systems always have lower surrogate recoveries in samples and blanks than what they obtain when running a curve. Some labs have overcome this by skewing down the surrogate recoveries QC limits (e.g. from 80-120 to 70-110; same window but skewed about 10% lower).

Final thoughts when using a 5890 or 6890 GC

- Use stainless steel nuts on GC to MSD interface. The brass ones can strip, causing leaks and other bigger problems. Agilent likes to sell the brass ones with the logic that it's better to have the \$10 brass nut strip than it is to have the interface strip. Our logic is that it's better to have neither strip.
- The splitless flow path on the 6890 is different than the 5890. As a result, it is often necessary to start runs at 50 °C or lower with the 6890. If you have a 6890 and start a run at >100 °C and are unhappy with the results, change the temperature programming to start at 50 °C for 1 minute, then ramp 20 °C to the temperature you would have started at. This often results in better chromatography.
- For volatiles analysis with a split/splitless injector and a 5890 GC, consider using a 0.32 mm guard column inserted into the injection port rather than the conventional “slice and dice” plumbing whereby the purge and trap transfer line is connected to the inlet line on the injector.

You'll need to butt connect a 6" piece of 0.32 mm guard column tubing to the purge and trap transfer line (with a 1/16" to 0.32 mm union) and insert the 0.32 mm guard column through the septum and into the injector until it is about 1/4" from the analytical column. This reduces contact of the volatile organics with stainless steel and we have seen numerous times where this improves performance.

For 6890 GCs, the conventional "slice and dice" plumbing works better.

- Never use graphite ferrules on detector end. Always use the longer high vespel content graphite/vespel ferrules (85% Vespel, 15% graphite) on the fitting into the mass spec.
- Use the Agilent "bullet" ferrules with shallow nuts on injector ports.
- Use UHP Helium and Indicating Moisture/Oxygen and Hydrocarbon traps. It's usually a good idea to remove the molecular sieve traps in the GC because they are not indicating so you have no idea of their condition. Instead, filter the carrier supply externally with indicating Moisture/Oxygen and Hydrocarbon traps.

Questions or comments on this or any issue of OPTIMIZE may be emailed to the author, Mark Ferry, at MFerry@SPEX.com.

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