Agilent Technologies
Innovating the HP Way

Optimizing the 6890 Series GC for High Performance MS Analysis

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Application Note

6890/5972, 6890/5973 GC/MS Systems

GC/MS AN 97-1

Abstract

Trace level GC/MS analysis requires a system that is performing at its best. Without a properly optimized GC, the mass spectrometer may not give the sensitivity expected. In other words, when more of the sample gets from the injection port to the ion source, the more likely a detector will produce a signal. Also, if the chemical noise from the GC is too high, the signal-to-noise ratio and ability to detect small analyte concentrations will be reduced. This note is a "how-to" guide for improving the GC performance. This will, in many instances, improve the overall performance of a GC/MS system. This guide is specific for the 6890 Series GC used with the 5973 MSD and the 6890 Series MSD.

Instruments

Agilent Technologies 6890/5973 and HP 6890/5972 were used.

Supplies

In order to improve the performance of the system, there are some supplies that should be on hand. These may not give significant improvements by themselves, but, when installed together, will give the best results. Many of the supplies which will be referenced have changed over the past few years and will probably continue to be improved. So, it is important to stay informed and purchase the most recent updated versions of the consumables.

The carrier gas line

The GC carrier gas should be at least 99.999% helium (called "five nines" helium). Lower grades of helium are available and can contain impurities that can damage the GC column (e.g., oxygen) and contribute to the chemical noise background. Even with a high purity gas there may be trace water, oxygen and hydrocarbons. Putting a trap in the carrier line will eliminate these contaminants (see Figure 1). The mass spectrometer gas purifier trap is recommended and shipped with

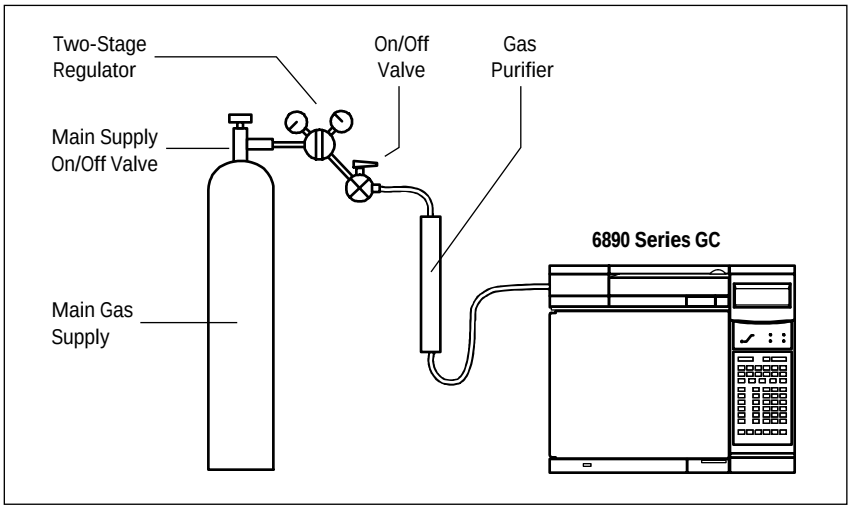

Figure 1. General gas plumbing assembly. The mass spectrometer gas purifier must be installed diagonally or vertically.

all new MSDs. It must be installed diagonally or vertically for optimum performance. **Do not install it horizontally**. High-purity helium also increases the effective lifetime of traps.

Pre-cleaned, refrigeration grade 1/8-inch copper tubing should be used with high quality carrier gas. Other tubing can be cleaned by running solvents (methanol, ethyl acetate, hexane) through it in a water aspirator vacuum set-up. The use of chlorinated solvents is not recommended due to possible long term contamination of flow lines and controllers.[1] Laboratory manifold systems, especially when new, tend to have hydrocarbon contaminants. Purging the new lines, before connecting the clean tubing to analytical instruments, is essential.

The supplies needed for the carrier gas line are

- ≥ 99.999% He: Gas supplier
- Clean copper tubing (50 ft): P/N 5180-4196
- Mass Spectrometer gas purifier: P/N 5182-3467

Splitless inlet consumables

The split/splitless inlet (Figure 2), has many consumable parts that should be kept on hand. Many of these consumables, such as liners (5), come in a variety of designs (Appendix A). The proper liner to use is very dependent on the application. For trace level analysis, the single tapered, deactivated liner is recommended. The Viton O-ring (4) holding the liner in place should be replaced periodically to reduce the chance of leaking. The seal and the washer in the bottom of the injection port (10, 11) should be replaced whenever the reducing nut (12) is removed. The recommended seal is gold plated to reduce metal catalyzed thermal degradation of analytes. Septa (2) should be replaced quite frequently: for example, every 100 injections. The low bleed, pre-cored, red septa should be used. Keeping a beaker of septa in an oven at 250°C at all times will eliminate the need to condition the septum once it is in place.

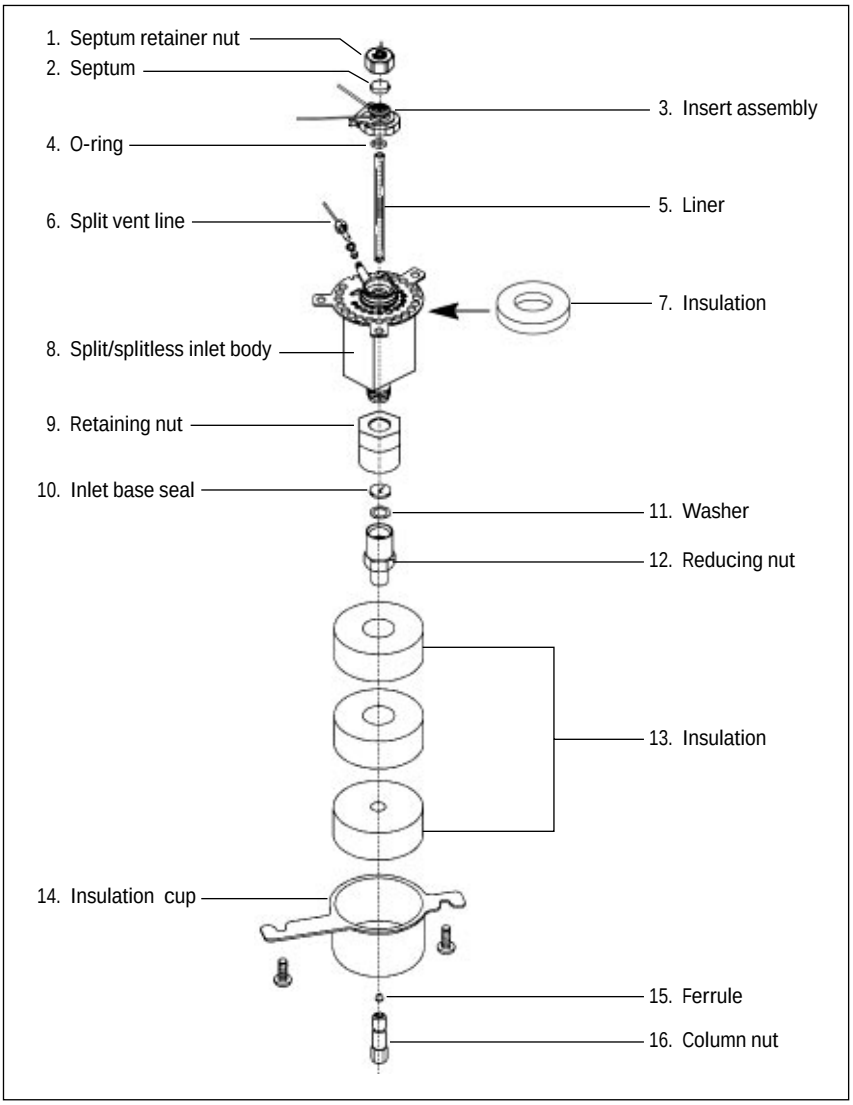

Figure 2. Split/splitless inlet assembly

A Merlin Microseal™ is highly recommended over a conventional septum nut and septum (1, 2). The Microseal™ eliminates the need for septa and lasts for tens of thousands of injections without leaking. It is most appropriate

with the Automatic Liquid Sampler (ALS) injection tower and only works with untapered, blunt tip syringe needles. The Microseal™ has been improved over the past year. Older seals have a maximum pressure rating of 30 psi. The new seals are rated to 100 psi. It is recommended that the new seal and nut be used. The gold nuts (stamped "303C") are not compatible with the new seals. A gray nut, stamped "221B," should be installed.

Electronic pneumatic control (EPC) is an integral part of the 6890 Series GC. The EPC version of the 6890 is required when using an 5973 MSD. The manual version of the 6890 or any version of the 5890 will not work with the 5973 MSD. Electronic control gives the best repeatability in retention time and area counts. Using the electronic pulsed splitless mode allows for complete transfer of larger volume injections (up to 5 µL) onto the column. Even larger volume injections (> 5 µL) may result in more inlet maintenance, especially with dirty samples.

The 6890 does have a new inlet that accommodates injections up to 250 µL. It is called the programmable temperature vaporizer (PTV). It works with the ALS to deliver large volume injections (LVI). The inlet works by venting the solvent before analysis. The analyte is trapped and concentrated. It is then delivered to the column as a single plug.

The list of splitless inlet consumables is

- Molded Septa (11 mm, red, 25/pk): P/N 5181-3383

OR

- High Pressure Merlin Microseal™ starter kit: P/N 5182-3442
- Merlin Microseal™ septum: P/N 5182-3444
- Merlin Microseal™ septum nut: P/N 5182-3445
- Liner, single taper, deactivated, no glass wool: P/N 5181-3316
- Viton O-ring (12/pk): P/N 5180-4182
- Gold plated seal: P/N 18740-20885
- Washer (to go with seal): P/N 5061-5869
- 10 µL Blunt needle syringe: P/N 9301-0713

Column consumables

The optimal choice of column is once again dependent on the application. For trace-level, high-sensitivity applications, a column with a thin film and low bleed is best. A 30 m, 0.25 mm ID, 0.25 µm film, 5% phenyl–95% methyl silicone column is a versatile column that can be used for many applications. Special low-bleed MS columns cost more but will give better results.

The proper column nut and ferrule combination are critical for a leak-tight seal. Newer column nuts may not be compatible with all ferrules. The proper ferrule will be dependent on column outer diameter and is specified below. The ferrule should only be slightly larger than the column outer diameter. The use of 100% graphite ferrules is not recommended as they are easily over-tightened causing graphite to extrude into the injection port. This will be apparent when disassembling the injection port. If there are pieces of graphite in the bottom of the injection port, the ferrule(s) was (were) over-tightened. The presence of graphite in a hot injection port can cause thermally labile compounds to degrade. It can also affect the chromatography and cause tailing. Thus, 10% graphite, 90% Vespel ferrules are highly recommended. Vespel ferrules will shrink as they are heated. Conditioning them for 4 hours in a 250°C oven will pre-shrink them before use. Alternatively, the column nuts (Figure 2, #16) can be retightened after the column oven cycles a few times.

The column, column nut and ferrules supplies are

- 30 m column, 0.25 mm ID, 0.25 µm, low bleed (HP-5MS): P/N 19091S-433
- Column nuts (wrench-tighten only) 2/pk: P/N 5181-8830
- Ferrules for 0.2 mm ID columns, 10/pk: P/N 5062-3516
- Ferrules for 0.25 mm ID columns, 10/pk: P/N 5181-3323
- Ferrules for 0.32 mm ID columns, 10/pk: P/N 5062-3514
- Ceramic scoring wafer (column cutter), 4/pk: P/N 5181-8836

A sharp column cutting tool is needed for making clean cuts. The ceramic scoring wafers or sapphire square edge pens are desirable. The diamond point pens are harder to use. Ceramic scoring wafers are extremely sharp. They should be used with care. An X-ACTO™ or Swiss Army knife **is not** a column cutting tool.

A 10x magnifier should be used to assure that the cut is clean and no column shards are lodged inside the column.

Interfacing the column to the MS

The column is connected to the mass spectrometer through an interface that is sealed with a column nut and ferrule. The specific ferrule used depends on the column diameter. A 100% graphite ferrule should never be used.[2] The ferrules required are 15% graphite, 85% Vespel. The column nut listed is brass; stainless steel nuts should never be substituted. Stainless nuts may damage the threads on the interface. Damaged threads cause air leaks and the entire interface has to be replaced.

The MS interface supplies are

- Brass column nut: P/N 05988-20066
- Ferrules for 0.2 and 0.25 mm ID columns, 10/pk: P/N 5062-3508
- Ferrules for 0.32 mm ID columns, 10/pk: P/N 5062-3506

Installation of Consumables

This section assumes that you are going to do a preventative maintenance (PM) on your 6890 Series GC. If this is a new GC/MSD system, many of these steps will be completed by an Customer Engineer during installation. Before beginning the preventative maintenance, please read this section carefully. Have on hand the 6890 Series GC site prep manual, the 6890 Series GC operating manual, the 6890 Series GC maintenance and troubleshooting manual and the MS hardware manual; they will be referenced frequently.

The manuals necessary are

- 6890 Series GC site preparation and installation manual: P/N G1530-90300
- 6890 Series GC operating manual: P/N G1530-90310
- 6890 Series GC maintenance and troubleshooting manual: P/N G1530-90320
- MS hardware manual (HP 5973 MSD): P/N G1099-90001

OR

- MS hardware manual (HP 6890 Series MSD): P/N 05972-90026

When all of the consumable supplies, previously mentioned, are at hand, a proper preventative maintenance can be completed. To begin a PM it is necessary for the GC zones to be cooled (oven, inlet, MS interface). The 6890 Series MSD has to be vented. Please refer to the MS hardware manuals for venting instructions (p. 52 for the 5973; pp. 58–59, for 6890 Series MSD).

Installation of gas supplies

Following the directions on pages 14–20 in the GC site preparation/ installation manual, install the gas line supplies. Care should be taken in making the Swagelok™ connections. The trap can be broken if too much stress is placed on the connection during tightening. Leak check all connections with a helium leak detector. (No Snoop™ please!) Make sure that all the lines are purged with helium before connecting them to the GC.

Installation of split/splitless inlet supplies

Before handling any of the injection port supplies, wash hands and/or wear lint-free gloves. Oils on the hands will be transferred to these parts and become background in the system, requiring extra bakeout time. Washing the hands is especially important after eating. Following the instructions in the GC operating manual (pp. 85–86), remove the septum nut, septum, and liner. Discard the septum, liner and liner O-ring. Open the oven door, loosen the 1/16-inch column nut and remove the column and nut. Remove the insulation cup and any necessary insulation (Figure 2, #14) to provide access to the reducing nut (Figure 2, #12). If the lower insulation cup was not in place, find it, because this piece improves the inlet temperature profile.

With a 1/2-inch wrench remove the reducing nut (Figure 2, #12). Due to heat cycling of the GC, the reducing nut will be very tight. Remove the seal and the washer (Figure 2, #10, #11) and discard. Place a new washer in the reducing nut and a new seal (flat side with groove up). Hand-tighten the reducing nut back into place within the retaining nut and then wrench-tighten until very tight. Replace the insulation cup. Insert a new liner and O-ring. The single taper liners are installed with the taper down, toward the column end of the inlet. Hand-tighten the insert assembly (Figure 2, #3). Add the Merlin Microseal™ or proper

pre-conditioned septum and septum nut. The molded septum is installed with the hole up. Follow the directions supplied with the Merlin Microseal™ to insur proper installation. If the green septum nut is used, wrench-tighten the weldment and septum nut with the septum nut wrench until the C-ring lifts off the top of the green septum nut.

At this point the inlet should be leak checked. Follow the directions in the GC maintenance and troubleshooting manual (pp. 39–42).

Column installation

Each column ships with a quick reference guide (HP P/N 5961-5652). Please read it before installing a new column. Working with fused silica columns may be dangerous. Wear proper eye protection. Inspect the column for damage or breakage. Unweave 0.5–1 coil of the column from its basket to make it easier to install. Push a septum onto the inlet end of the column about 10 cm. Put the column nut and appropriate ferrule on the column. Cut 5–10 cm off the inlet end of the column. Check the cut with a 10x magnifier, the cut should be straight, not jagged, with no column shards within the column. If the cut is jagged or shards are inside, try again. After a clean cut is obtained, mark the proper column position with the septum (Figure 3). The septum will hold the column nut and ferrule in place. Place the column on the column hanger. Insert the column nut into the inlet reducing nut and finger-tighten. Wrench-tighten the column nut. The column should be stationary in the ferrule. Carefully slide the septum down away from the nut without disturbing the column positioning. The septum can be left in place if desired.

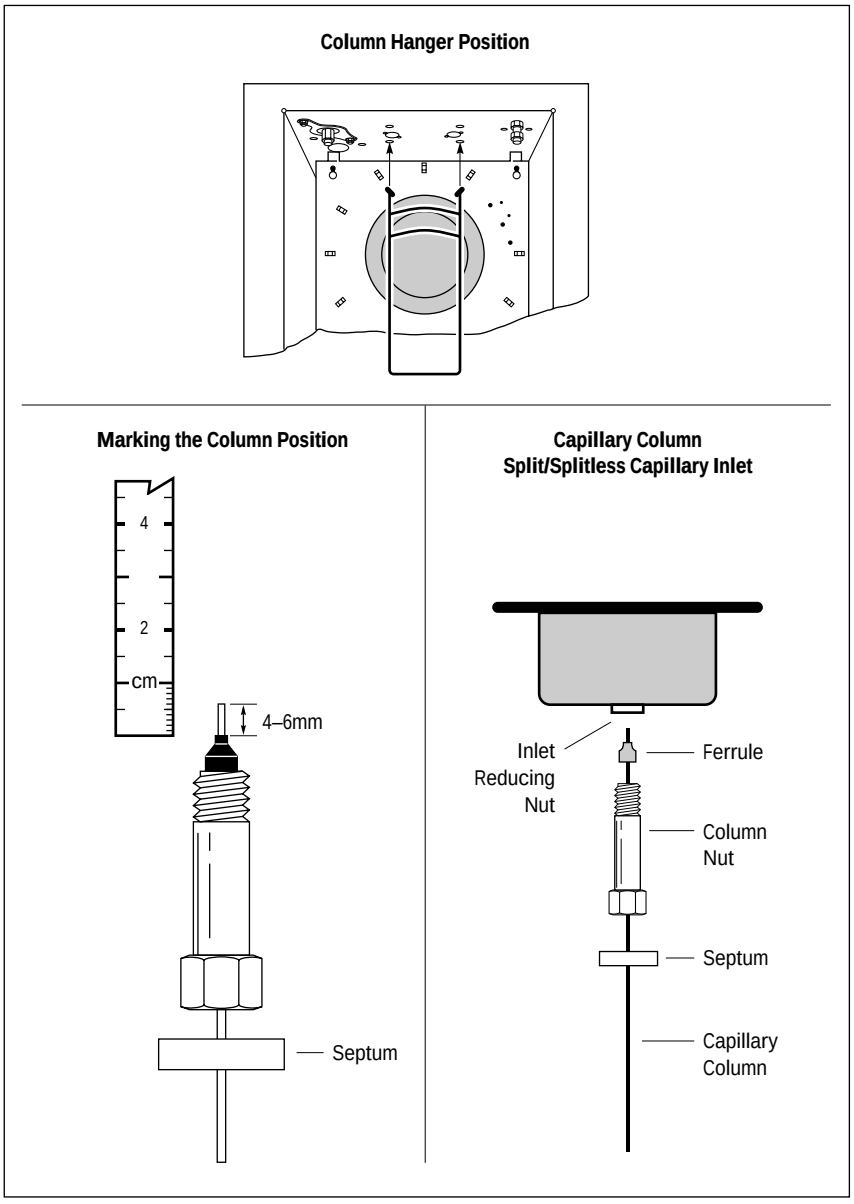

Figure. 3 Proper installation of capillary columns in split/splitless inlet

Using the GC keypad or the MS ChemStation software, input the Column Dimensions, set Outlet Pressure to Vacuum and Column Flow between 1 and 1.5 mL/min helium (Table 1). The Split Vent Flow should be approximately 50 mL/min. These parameters are accessed through the inlet and column screens. Place the detector end of the column into a beaker of water and check for bubbles to show helium flow. Heat the injection port. When the

injection port reaches the setpoint temperature, retighten the column nut in case it loosened. Check once again for column flow. Remove the end of the column from the beaker and close the oven door. **Condition the column by slowly (5°C/min) ramping it to its maximum operating temperature. Leave it at that temperature for least 2 hours; overnight is preferable.** The maximum operating temperature for an HP-5 column is 325°C. Cool the oven to ambient and insert the interface nut and ferrule onto the column. Properly cut off 5–10 cm of the column. Properly place the column into the interface by following the directions in the MS hardware manual (pp. 26–29 for the 5973; pp. 24–25 for the 6890 Series MSD). Hand-tighten the interface nut and then wrench-tighten the nut. The nut should be tightened only until you hear two squeaks. This is a firm seal. Pump down the detector as directed by the MSD manual (pp. 36–37 for the 5973; pp. 36, 40–41 for the 6890 Series MSD). Keep the oven at ambient temperature until the source is hot. Check the interface connection after the interface is heated. The interface nut may need additional tightening.

Tips for Better Method Performance

Numerous splitless parameters need to be optimized for the best splitless injection. Table 2 (below) summarizes them.

The proper inlet temperature is needed to evaporate high boiling point compounds without thermally degrading other compounds. Normally, the inlet temperature is a compromise between these two factors. A good starting point is 250°C.

Liner design is one of the most difficult choices simply because of the variety of liners available. The features that are most important in a liner are the volume, whether it is deactivated or not, and whether or not it contains deactivated glass wool. As a general choice for high sensitivity work, a 4 mm single tapered, deactivated liner with no glass wool is recommended. For large volume injections (≥ 2 µL) and for the highest repeatability (especially with small volume injections of ≤ 0.5 µL[3]), deactivated glass wool is necessary. For dirty samples deactivated glass wool helps to keep the non-volatiles from getting to the column, but too much deactivated glass wool can greatly decrease sensitivity. Often, the most appropriate liner must be determined through experimentation. Please note: Removing and/or breaking deactivated glass wool **creates** active sites.

Splitless valve timing is critical. The ON time (splitless mode) should to be long enough to assure that all of the injected sample reaches the column.

A textbook splitless injection has the liner volume swept at least two times (during the "ON" time). A 4 mm liner has an approximate volume of 1 mL. With a GC/MS flow rate of 1 mL/min, a two minute splitless injection would be necessary.

Table 1. Head Pressures and Calculated Flowrates for a Splitless Inlet at an Oven Temperature of 25 °C with the Outlet Pressure set to Vacuum

Column Inner Diameter (mm)	Length (meters)	Head Pressure (psi)	Linear Velocity (cm/sec)	Column Flow (mL/min)
0.20	12	6.0	57	1.0
0.20	25	15.0	39	1.0
0.20	50	28.0	28	1.0
0.25	30	6.2	36	1.0
0.32	30	3.4	50	2.0
0.32	50	5.5	34	1.5

Table 2. Splitless Parameters

Injection port temperature	Column flow
Liner design	Solvent
Sample volume	Sample volatility
Splitless valve time	Injection speed

However, this long splitless time has not been common. There are two reasons for this. (1) Conventional (manually controlled) split/splitless inlets were pressure regulated (constant pressure, regardless of oven temperature) and not flow regulated (changing pressure with oven temperature), so a higher-than-optimal flow was set initially so that the flow did not go to zero at high oven temperatures. Thus, a typical splitless or "OFF" time has been between 0.5 to 1.5 minutes. (2) Liner volumes smaller than the textbook examples have typically been used. Since a 2 mm liner (250 µL volume) was more commonly employed, the splitless time was proportionally shorter.

Finally, with the programmable control afforded by EPC, flows can be reliably pulsed during the injection process. With pulsed splitless injections, flows during the splitless time can be 2–6 mL/min, resulting in splitless times less than 2 minutes for a 4 mm ID liner. The pulsed splitless injection mode on the 6890 is recommended for GC/MS work. After the injection pulse, the system returns to analytical flow rates of 1–4 mL/min He. The highest flow allowable depends on the MSD. Refer to the appropriate MS hardware manual for your detector's limit.

Unless all analytes have high boiling points, the initial oven temperature should be set to take advantage of the solvent effect. The solvent effect focuses the analytes on the head of the column. The oven temperature should typically be set to ≥ 10°C below the boiling point of the solvent used (Table 3). On the other hand, the MS interface

Table 3. Boiling and Initial Oven Temperatures for Common Solvents

Solvent	Boiling point (°C)	Initial oven temperature (°C)
Diethyl ether	36	10 to 25
n-Pentane	36	10 to 25
Methylene chloride	40	10 to 35
Carbon disulfide	46	10 to 35
Acetone	56	25 to 45
Chloroform	61	25 to 50
Methanol	65	35 to 55
n-Hexane	69	40 to 60
Ethyl acetate	77	45 to 65
Acetonitrile	82	50 to 70
n-Heptane	98	70 to 90
Isooctane	99	70 to 90
Toluene	111	80 to 100

temperature should be hot enough to avoid loss of analytes on cold spots. The interface should be set to the maximum oven temperature for the analysis or 10–15°C higher if the upper temperature limit for the column is not exceeded. The default method temperature is 280°C; the interface temperature should be optimized as part of method development.

Finally, the rate of auto-injection of a sample has been studied for splitless injections. It has been found that fast injections, such as with the ALS, tend to give the most repeatable and non-discriminating results.

Using Pulsed Splitless Injections

Pulsed splitless injections are the best way to do splitless injections. Electronic pneumatic control of the splitless inlet allows for high flow rates initially, followed by more typical GC/MS flow rates. A pulsed splitless injection transfers more of the sample onto the column and allows for increased injection volumes up to 5 µL. When the injected volume is flash vaporized, the required expansion volume for the solvent is greatly increased. (Solvent choice also effects expansion volume.) The use of higher initial inlet pressures reduces the volume ($P_1V_1 = P_2V_2$) so the entire injected volume can move to the column. The higher pressure also decreases the likelihood that highly volatile compounds will escape out the top of the injection port through the septum purge vent (Figures 4 and 5). In the case of thermally labile compounds, the faster they leave the hot injection port the less

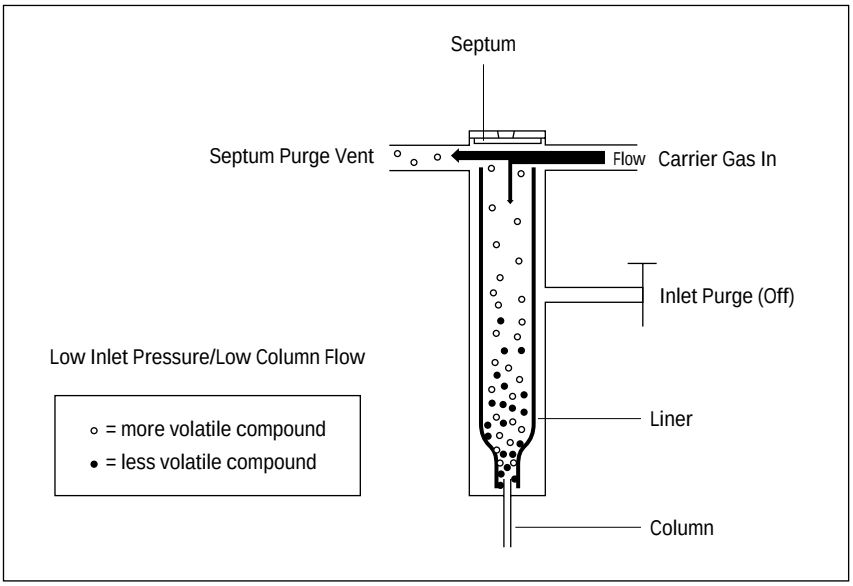

Figure 4. A low initial inlet pressure causes loss of volatile compounds.

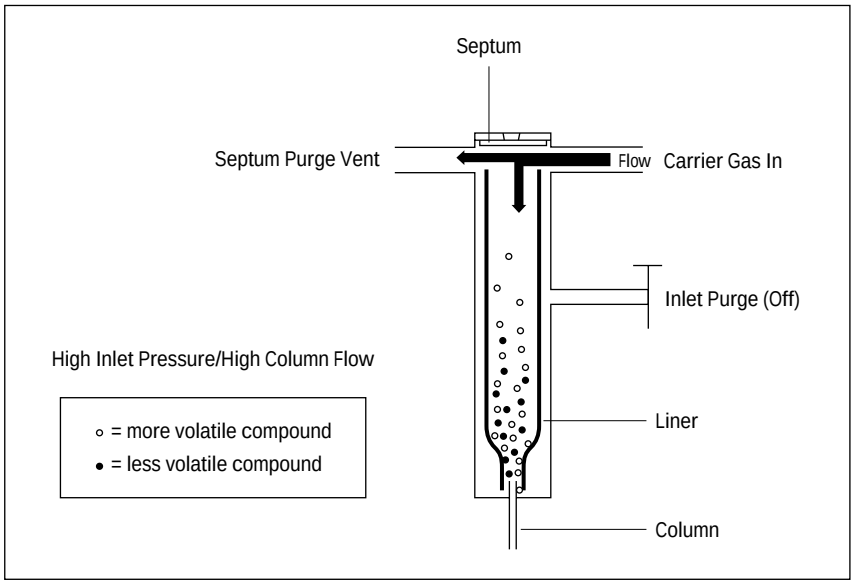

Figure 5. With the correct inlet pressure there is no loss of volatile compounds.

likely they are to degrade.[4] The flow rate is then reduced to the value desired for the chromatographic separation. This flow is held constant by increasing the pressure as the oven temperature increases. Figure 6 is a graphical representation of the pulsed splitless technique with constant flow. Pulsed splitless injections should always be used when sensitivity and/or repeatability are critical. Refer to pages 99–100 in the GC operating manual for how to set up a pulsed splitless injection.

Electronic pressure and flow control of carrier gases not only help with larger volumes, they also help to decrease run times and maintain stable MS sensitivity by keeping the carrier gas flow constant. These lead to a shorter analyses, higher sensitivity and higher reproducibility. The benefits for the analyst are more chromatographic analyses per shift, better data and higher revenues per instrument.

Summary

Following the instructions in this guide will improve analytical results with your GC/MSD system. Contamination interferring with the determination of your analytes will be minimized and sample transfer optimized, both improving sensitivity.

A final note: the choice of vials and septa will affect your results. Screw cap vials are not recommended for GC/MS analyses. Application note 228-244, "Effects of Vial Septa Used in GC/ECD Analysis of Trace Organics," P/N 5091-8980, will help you make the right choice.

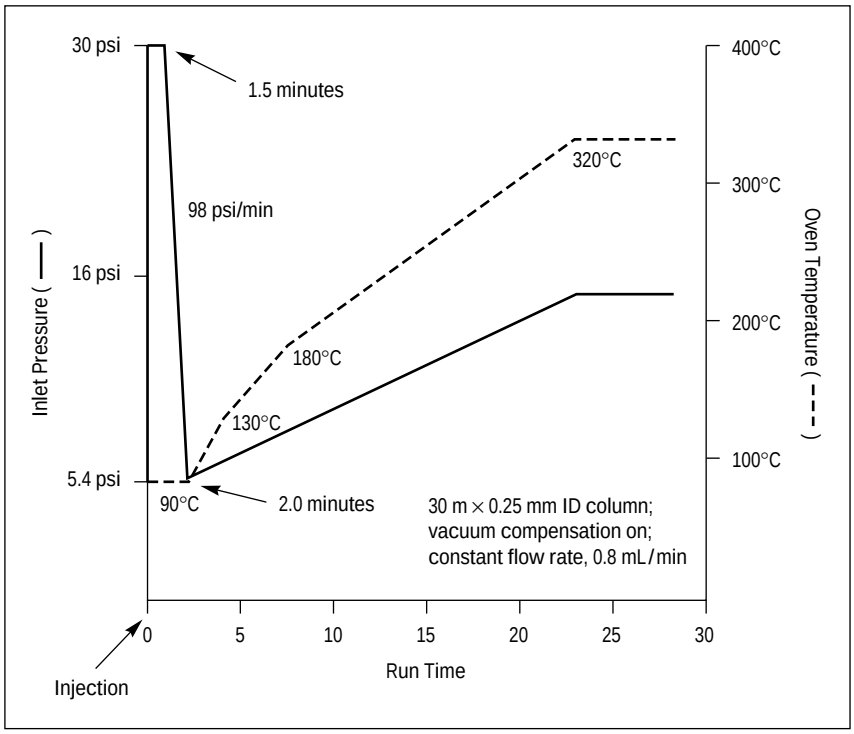

Figure 6. The pulsed splitless injection technique employing constant flow with electronic pneumatic control (EPC). This technique allows larger injection volumes and inhibits the loss of volatile compounds out of the septum purge vent.

References

1. Another commonly used cleaning technique is to heat the copper tubing with a Bunsen burner, propane torch or heat gun while helium is flowing through the tubing. This is done after connecting the tubing to the helium supply but before connecting it to the GC. This process bakes off all the volatile contaminants. Safety precautions should be taken if this procedure is done.
2. Similar to the injection port, pieces of graphite may extrude into the interface and contaminate the MS.
3. Reviewed in an MS Applications Brief MS 95-1: **Analyzing aromatics in reformulated gasoline by GC/MS,** P/N (23) 5964-0116E.
4. A excellent example of this can be found in the 1995 Pittsburgh Conference paper #347: **Improving the Analysis of Pesticides by Optimizing Splitless Injections,** Philip L. Wylie et al., Hewlett-Packard Co. The complete article can be found in the Journal of Official Analytical Chemistry International (JAOAC Int.) as **Improved Gas Chromatographic Analysis of Organophosphorous Pesticides with Pulsed Splitless Injection,** Philip L. Wylie and Katsura Uchiyama, Hewlett-Packard Co., Volume 79, Issue 2, pp. 571–577, 1996.

Appendix A

Capillary Inlet System Liners

LINER	PART NO.	PRICE	CONFIGURATION: ID VOLUME	CONFIGURATION: GLASS TYPE	CONFIGURATION: DEACTIVATED	CONFIGURATION: GLASS WOOL PACKING**	APPLICATIONS: FAST INJECTION (7673 ALS): SPLIT	APPLICATIONS: FAST INJECTION (7673 ALS): SPLITLESS	APPLICATIONS: SLOW & MANUAL INJECTION: SPLIT	APPLICATIONS: SLOW & MANUAL INJECTION: SPLITLESS	LINER SEALS: FLUOROCARBON (MAX 350°C)	LINER SEALS: GRAPHITE (350°C AND ABOVE)
Single-Taper Liner	5062-3587	34	4 mm (0.8-mm end) 900 µL	Borosilicate	YES	YES**	C	●	C	●	5180-4182 (12/pk) 12	5180-4173 (12/pk) 48
Single-Taper Liner	5181-3316	31	4 mm (0.8-mm end) 900 µL	Borosilicate	YES	NO	—	A	—	●	5180-4182 (12/pk) 12	5180-4173 (12/pk) 48
Double-Taper Liner	55181-3315	34	4 mm (0.8-mm end) 800 µL	Borosilicate	YES	NO	—	A	—	●	5180-4182 (12/pk) 12	5180-4173 (12/pk) 48
Split/Splitless Liner	19251-60540	26	4 mm 990 µL	Borosilicate	NO	YES**	●	D	●	D	5180-4182 (12/pk) 12	5180-4168 (12/pk) 48
Split Liner	18740-60840	46	4 mm with cup	Borosilicate	NO	YES + column packing	—	—	E	—	5180-4182 (12/pk) 12	5180-4168 (12/pk) 48
Split Liner	18740-80190	41	4 mm with cup	Borosilicate	NO	NO	—	—	●	—	5180-4182 (12/pk) 12	5180-4168 (12/pk) 48
Splitless Liner	18740-80220	27	2 mm 250 µL	Quartz (Purity 8)	NO	NO	—	A,B	—	B	5180-4182 (12/pk) 12	5180-4173 (12/pk) 48
Splitless Liner	5181-8818	30	2 mm 250 µL	Quartz (Purity 8)	YES	NO	—	A,B	—	B	5180-4182 (12/pk) 12	5180-4173 (12/pk) 48
Direct Liner	18740-80200	17	1.5 mm 140 µL	Borosilicate	NO	NO	—	A,B	—	B	5180-4182 (12/pk) 12	5180-4173 (12/pk) 48

A. Can be used without the glass wool in some applications, but liners with glass wool are generally recommended for best reproducibility in fast injections.

B. Recommended only for small (< 0.5 µL) volumes, depending on solvent and conditions.

C. The glass wool packing as supplied may not provide adequate mixing for good precision in split injections. Liners can be packed with silanized glass wool positioned as in the straight 4 mm split/splitless liner, part no. 19251-60540.

D. Taper liners are recommended for best performance in this application, particularly with labile samples and wide-boiling-range mixtures.

E. Not recommended for use with electronic pressure control.

● General recommendation

○ See notes at left regarding use

* Quality discounts available; please inquire.

** Silanized glass wool, 10 gm, (pesticide grade) (HP part no. 5181-3317).

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