2
Basic Overview on Gas Chromatography Injectors

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2.1
Introduction

Numerous injection techniques are used in capillary GC. The injection port has been constantly optimized to allow higher accuracy in terms of retention time and response area. Despite the fact that the GC column is the "heart" of the separation, the injector remains, probably, the most critical part. If correct vaporization and focusing on the column is not achieved, the consequences are devastating, regardless of the success of the GC separation. GC injection parameters (amount, solvent, splitting or not, nature and volume of the liner, injector temperature, injection velocity, etc.) should be properly optimized in order to ensure an accurate GC separation. So far, the classical split/splitless injectors remain the most widely used in the majority of GC instruments. It is also important to mention on-column injectors, but the programmed temperature vaporization (PTV) injector is the most used, given its versatility and usefulness. Among the various injection modes, this chapter will highlight particularly solid-phase microextraction (SPME) [1].

2.2
Injectors

2.2.1
Split Injector

Split injection is the oldest and most common injection technique used to inject 1–5 μl of sample into a heated injection port. Samples are vaporized rapidly, and approximately 1–2% of the vapor enters the column. The remainder of the vaporized sample passes out through a split or purge valve. Split ratios vary from 1 : 10 to 1 : 100. Column temperature is usually 20–30 °C above the boiling point of the injection solvent. Split injection is a simple technique used to control the split ratio by opening or closing the split (purge) valve. A typical split

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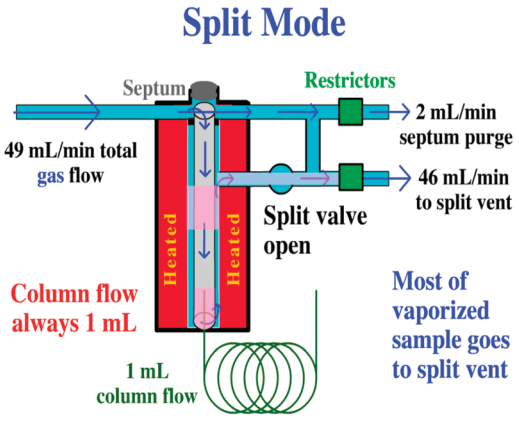

Figure 2.1 Schematic diagram of an injector in split mode. The total gas flow (1) through the column (green at the bottom), (2) out of the septum purge, and (3) out of the split vent (add up to the incoming flow, 49 ml/min in this example). So 1 + 2 + 46 = 49 ml/min. The split ratio is 1/49 because 49 parts are injected and 1 part goes onto the column (http://www.shsu.edu/~chm_tgc/primers/pdf/GC.pdf).

injector is shown in Figure 2.1. This technique is particularly suitable for analyzing pure or concentrated samples. Trace analysis is difficult due to fractional sample transfer to the column and splitting discrimination in favor of the high molecular weight solutes [2–4].

2.2.2 Splitless Injector

In splitless injection, the split valve is initially closed and the vaporized sample components condense in the first few centimeters of the column with an approximate flow rate of 1 ml/min. The initial column temperature is maintained 10–20 °C below the solvent boiling point and is programmed. After 45 s, the split (purge) valve opens, and all residual vapors are swept out at a flow rate of 50 ml/min. This purge delay is traditionally chosen to be between 0.5 and 2 min. The longer the purge delay, the greater the sensitivity, and the larger the peak width. Therefore, it is desirable to optimize both the initial column temperature and the time to open the split valve. Splitless injection is highly recommended for trace analysis of environmental, pharmaceutical, and biomedical samples. A typical splitless injector is shown in Figure 2.2.

Some technical aspects should be considered for a successful outcome of split/splitless injection as follows:

- The vaporizer chamber/injector must have a volume of 1 ml for a 1–2 µl injection.
- The flow rate should be 2–4 ml/min for conventional splitless injectors with a narrow bore analytical column.
- A splitless period of 45 s is needed to transfer a 3 ml volume.

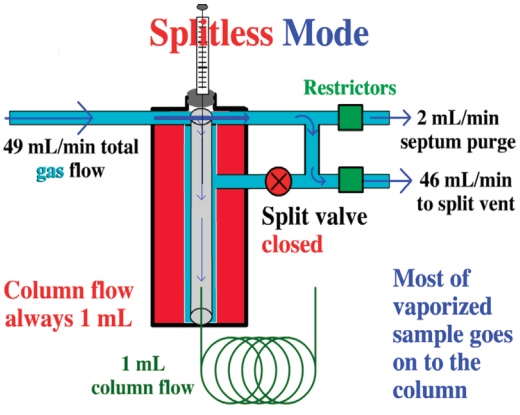

Figure 2.2 Schematic diagram of an injector in splitless mode. The entire analyte sample vaporized in the injector goes onto the column without split. Therefore, the method can be considered as more sensitive. (http://www.shsu.edu/~chm_tgc/primers/pdf/GC.pdf).

- The split ratio should be maintained at 1 : 10–1 : 25.
- A 1–2 µl injection volume is generally used for a splitless injection [4–9].

A typical configuration for moderately polar analytes or ultrahydrophobic contaminants analysis is a 1–2 µl injection volume, 200–250 °C injection temperature, splitless period of 0.5–2 min, and a starting oven temperature of 70–90 °C for 1–2 min.

If an injection port is composed of a glass liner and glass wool, it may contain many active sites, from silanol or the metal ions. At high temperature, the active sites tend to adsorb and/or degrade analytes, resulting in smaller peak sizes and/or tailing peaks. In order to avoid degradation of thermally unstable compounds and to enable a faster transfer of the analyte, it is recommended to use a pulsed splitless injection by applying pressure during the splitless period.

2.2.3 Liners

The liner plays an important role in converting liquid samples to vapor and is introduced before the separation column. The main function of the liner is to ensure a rapid, uniform vaporization and an efficient transfer to the head of the column without secondary interactions. If the sample does not transfer efficiently onto the column, peak tailing or splitting may occur. However, understanding the function of the liner simplifies the selection process, leading to improvements in peak shape and method robustness.

The liner should be selected depending on its internal diameter, shape, and coating. Liners with a larger internal diameter are better for high solvent capacity, as they decrease the possibility of discrimination and sample loss. Liners packed with an adsorbent help minimize the loss of volatiles during solvent elimination. There are various types of packing material, including VolaspherA2, Chromosorb® W, glass wool, PTFE wool, Dexsil, and Tenax.

2.2.3.1 The Internal Diameter of the Liner

The internal diameter of the liner is an important factor to be considered. It should be adjusted with the volume of vapor produced by the solvent. The liner volume must be sufficient to accommodate the gaseous sample. If the diameter of the liner is too small, the sample will expand beyond the capacity of the liner, causing analyte loss through septum purge flow and split line. Often, this will lead to peak tailing or poor reproducibility. If the diameter of the liner is too big, there will be a large dead volume, which will increase the sample transfer time, leading to peak tailing. The amount of vapor volume depends on the solvent used, the temperature of the inlet, and the pressure inside the liner.

To calculate the vapor volume produced by a sample, we use the ideal gas equation:

$$\text{Vapor volume (ml)} = \frac{(V \times D/\text{MW}) \times R \times T}{P_\text{a} + \text{P}_\text{i}} \times 10\,00\,000,$$

where V is sample volume (ml), D is solvent density (g/ml at 20 °C), MW is molecular weight of the solvent (Da), R is Boltzman's gas constant (8.314462), T is inlet temperature (K), P_a is atmospheric pressure (Pa), and P_i is inlet pressure (Pa).

For a 1 µl injection of hexane at 300 °C and 66 KPa, the formula would be as follows:

$$\text{Vapor volume (ml)} = \frac{(0.001 \times 0.659/86) \times 8.314462 \times 573}{101325 + 66000} \times 10\,00\,000 = 0.22\,[10]$$

2.2.3.2 Liners for Split/Splitless Injections

After ensuring that the liner has the correct internal diameter, the next thing to be considered is the injection mode. If the injection is in split mode, then a linear liner is used. On the other hand, for splitless mode use a liner tapered at the bottom. Both split and splitless liner are shown in Figure 2.3.

After selecting the injection technique, the final thing to take into consideration is whether to use a packed or unpacked liner. Different types of liners are available, based on their packing material.

FocusLiner: This is a packed liner using deactivated quartz wool, named FocusLiner, which provides good peak shape and injection reproducibility with little low- or high-boiling point discrimination.

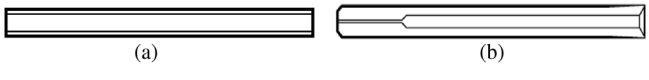

Figure 2.3 Typical split (a) and splitless (b) liner used in GC injection port.

Siltek-coated liners: Siltek liners are suitable for use with very active compounds, such as pesticides. They provide an even more inert surface than the normal deactivation process. These can be particularly useful for the analysis of very labile compounds, for example, endrin. These liners are available in both split and splitless formats.

CarboFrit liners: CarboFrit liners offer the same advantages as FocusLiners, but with higher inertness and temperature stability. They also have a Siltek coating, so they may be used with highly labile compounds [10].

2.2.4 On-Column Injector

On-column injection means direct injection in the head of the capillary column, without using any septum, avoiding the hot injection port. After injection, the cold injector is rapidly heated and the sample is vaporized and passed through the column. This technique requires thick film capillaries, a wide-diameter (0.53 mm, ID) megabore column, and a faster than normal flow rate (~10 ml/min). A typical on-column injector is shown in Figure 2.4. The main advantages come from the fact that the sample is introduced into a cold injector, which makes it suitable for analyzing thermolabile compounds. Because the entire sample is directly vaporized in the column, it allows a nondiscriminative transfer of the sample components into the GC system and provides very precise and sensitive quantification of trace analytes. However, it requires additional column maintenance with the gradual accumulation of nonvolatile sample components at the top of the column from one injection to another. One way to overcome this problem is to use a replaceable retention gap before the analytical column. On-column injection is commonly used in the analysis of relatively clean water samples.

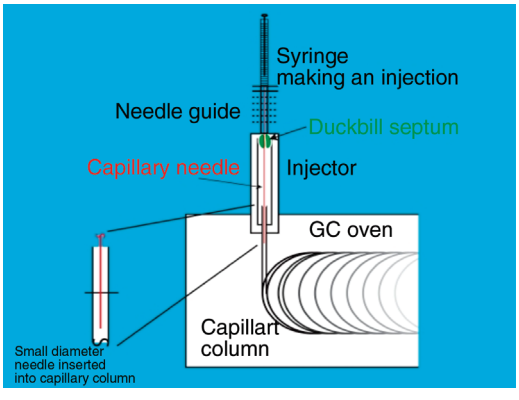

Figure 2.4 A typical on-column injector fitted with GC column (http://www.shsu.edu/~chm_tgc/GC/GCinject.html).

2.2.5
Solvent-Free Solid Injector

Using a solvent-free solid injector (SFSI) to directly introduce the sample into the column instead of using a conventional syringe-based sample injector is an example of a direct sample introduction method. Based on this concept, SFSI has been introduced utilizing a Keele injector (an injector developed initially for the analysis of the biological constituents of insect glands) coupled with mass spectrometry. The method eliminates the need for solvent extraction or purification procedures [11].

Samples are cut into small size pellets and 1 mg of sample is introduced into a glass capillary tube (1.2 mm ID × 30 mm length). Both ends of the tube are sealed briefly using a flame. The tube is then placed in a modified Keele injector. After heating the injection port for about 5 min, the tube is crushed by lowering the injector plunger and the sample analyte is carried into the GC column by the carrier gas. The SFSI is maintained at the injection port during the preheating phase, until the injector plunger reaches the top of the injector septum. This allows for a constant pressure of carrier gas to be maintained during analysis. The optimal conditions for SFSI are usually attained by sequentially varying one experimental parameter, while all other parameters are being kept constant. The parameters are allowed to vary in the following order: the injector temperature (200, 250, and 300 °C), preheating time (3, 5, 7, and 10 min), and holding time (0, 3, 5, 7, and 10 min) [12].

Therefore, SFSI can be used to isolate and extract volatile flavor components from any natural matrix. A solvent-free solid injector is illustrated in Figure 2.5.

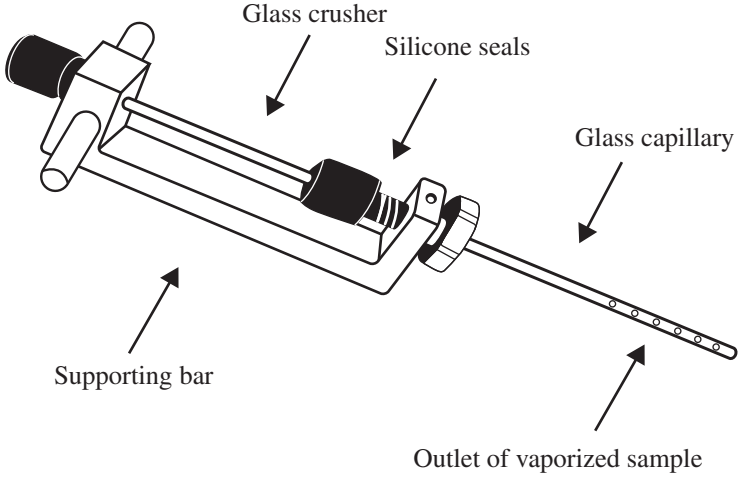

Figure 2.5 Illustration of a solvent-free solid injector SFSI [11].

2.2.6
Programmed Temperature Vaporization Injector

Due to the problem of contamination that may appear in the case of on-column injections, Vogt *et al.* in 1979 introduced the programmed temperature vaporization (PTV) injector, which retains nonvolatile compounds in a vaporizer chamber that does not reach the analytical column. The PTV inlet is considered a temperature programmable split/splitless inlet and has the same basic configuration. The sample is introduced into the inlet with the inlet temperature near the boiling point of the solvent and with a relatively high split ratio. The solvent and low boiling solutes are vented, while the higher boiling solutes remain and are concentrated at the inlet. Afterward, the split vent is closed, and the inlet temperature is increased, in order to transfer the solutes and any residual solvent to the column, for separation. Because the sample is evaporated in the inlet, nonvolatile sample components and degradation products remain in the inlet, minimizing column contamination. This technique avoids thermodegradation and loss of low volatile compounds. The main advantage of PTV is that the sample is placed in the injector, not in the column, and the nonvolatile compounds do not enter the column. Therefore, it is possible to use a large-volume injection, which potentially decreases detection limits. A schematic diagram of a PTV injector is shown in Figure 2.6. As much as 1 ml of sample can be introduced into the GC system in solvent split mode, enhancing the sensitivity of the overall analytical method and making the PTV injector applicable for online coupling of the GC with various enrichment techniques [13–18].

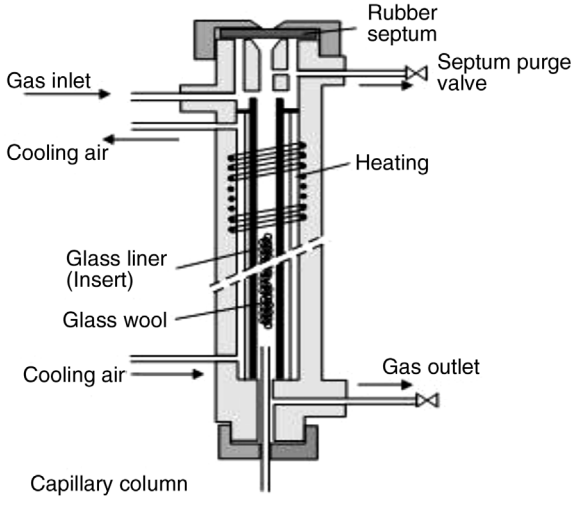

Figure 2.6 Schematic diagram of a PTV injector (http://chemicalanalysissecondedition.blogspot.kr/2012/11/injectors.html).

2.3 Injection Modes

2.3.1 Headspace (Static and Dynamic)

The "headspace" is the gas space above the sample in a closed vial. Volatile sample components diffuse into the gas phase, forming the headspace gas. A small volume of the headspace is injected into the GC, and this type of injection can be automated. Finally, the sample is loaded onto the column for chromatographic separation.

In the case of static headspace, the sample is sealed into a vessel, warmed, and then a sample of the atmosphere surrounding the sample is withdrawn and injected into the injection port of the GC.

Dynamic headspace sampling is a technique that uses a flow of carrier gas that passes through the sample vessel. This way, the headspace sample size is increased and, with it, the sensitivity of the analysis. Instead of allowing the sample to equilibrate in a sealed container, the sample is warmed and the headspace atmosphere is constantly purged out of the sample vessel through a trap.

Here the analytes are collected, as in a purge and trap analysis, while the carrier gas is vented. After the collection step, the trap is heated and backflushed to transfer the sorbed compounds to the GC for analysis.

Complex sample matrices, which would require sample extraction or preparation, can be analyzed directly using the headspace injection method, by placing them in a vial, with little or no preparation. This saves time, labor, and cost. Headspace GC is used to analyze volatile and semivolatile organics in solid, liquid, and gas samples. Nonvolatiles and semivolatiles are not detectable with this technique due to their low partitioning in the gas headspace volume. Since no solvents are used in sample preparation before GC, there is no solvent peak, no dilution of the compounds of interest, and no waste solvent to discard.

2.3.2 Solid-Phase Microextraction

Solid-phase microextraction is a solvent-less technique, which has been quite revolutionary for GC. It was developed by Janusz Pawliszyn in 1989 [19]. It is a simple solvent-less extraction procedure in which a fiber (coated on the outside with an appropriate stationary phase) can be immersed in the liquid sample or suspended in the headspace. The analytes are partitioned on the fiber coating. The analyte sorbed on the fiber phase is then desorbed in the injection port of the GC and transferred onto the column.

The extraction can be accomplished using headspace SPME or direct immersion SPME. In headspace SPME, the fiber is exposed to the vapor phase above the gaseous, liquid, or solid sample. In direct immersion SPME, the fiber is directly immersed in the aqueous sample. A degree of sample agitation is

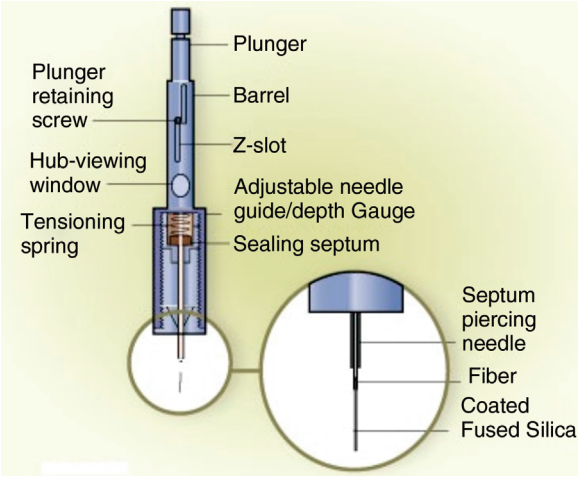

Figure 2.7 First commercial SPME device (Supelco) (www.chromedia.org/chromedia?waxtrapp=ujuipDsHqnOxmOllEcCnByFfG&subNav=abffyDsHqnOxmOllEcCnByFfGH).

needed, in order to increase the equilibration rate. After extraction, the fiber is withdrawn from the needle, and the needle is removed from the septum and inserted directly into the injection port. A typical SPME device is shown in Figure 2.7. The analyte is desorbed by heating the fiber and then the analyte is transferred directly to the column for analysis [20–24].

Efficient thermal desorption in GC depends on analyte vapor pressure, fiber type, injection depth, injector temperature, and exposure time. Most modern GC instruments are suitable for direct fiber introduction. A narrow-bore GC injector is required in order to ensure a high linear flow. Split/splitless injectors should be operated in splitless mode. The optimal desorption temperature is equal to the boiling point of the least volatile compound, and the GC column temperature should be kept low or with cryofocusing.

2.3.3
Purge and Trap

The purge and trap (P & T) method, developed by Bellar and Lichtenberg (1974), is a frequently used preconcentration device for the extraction of volatile organic compounds (VOCs) from a solid or liquid matrix for introduction into a GC [25]. The VOCs are concentrated in an absorbent trap, followed by thermal desorption into the GC. The purge gas (helium or nitrogen 99.999% purity) passes through the bottom of a fritted sparge vessel before contact with the sample. The frit disperses the gas into finely divided bubbles, creating a large surface contact area for the sample. This process allows the inert gas stream to strip the analytes from the sample matrix and concentrate them into the sorbent trap.

The purge efficiency of an analyte is based on vapor pressure, solubility, sample temperature, and purge volume. The higher the vapor pressure of the analyte, the quicker it vaporizes and leaves the sample. Highly polar organic compounds are quite soluble in water and are held together by very strong dipole–dipole interaction and hydrogen bonds. These compounds will have poor purge efficiencies. The purge efficiency of highly polar organic compounds can be increased by increasing the temperature, breaking the dipole–dipole interactions. The total amount of VOCs removed from the sample is directly proportional to the purge volume (purge flow rate and purge time). The recommended setting for the system is a flow rate of 40 ml/min for a period of 11 min for a purge volume of 440 ml.

The desorption mode requires the heating and backflushing of the trap with desorption gas, in order to release and transfer the analytes of interest to the GC. The GC carrier gas is used as the desorb gas and the process involves switching the six-port valve to place the trap in line with the GC column. The trapping material (adsorbents) efficiency is greatly affected by temperature and desorption time. The two most widely used adsorbent traps are the three-stage Tenax/silica gel/charcoal and the Vocarb 3000.

The purge efficiency is based only on the amount of analyte recovered from a purged sample, while the percent recovery takes into account both desorption and transfer efficiencies. The percent recovery is calculated as follows:

$$\% \text{ Recovery} = A/B*100,$$

where A is the area counts of analyte by purge and trap and B is the area counts of analyte by direct injection.

The trapping material is cleaned up using the trap bake mode prior to the next run. Baking a trap is analogous to baking a GC column. This process requires switching the six-port valve, allowing the trap to be flushed with purge gas [25–27].

2.3.4
Large-Volume Injection Mode (in On-Column or in PTV Format)

The large-volume injection technique (LVI), sometimes referred to as direct sample introduction (DSI), has been developed in order to increase the sensitivity and to separate the analyte from the dirty matrix coextract. It is commercially automated in a technique called difficult/dirty matrix introduction (DMI) [28–36]. A drawing of a DSI device that has become commercially available as the ChromatoProbe and a DMI liner is shown in Figure 2.8 [28,37].

LVI involves the following steps: (i) transfer of a sample (30 µl crude extract can be used) aliquot into a microvial located in a special holder (adapted glass injector liner). (ii) The solvent is evaporated and vented at a relatively low temperature. (iii) The injector is ballistically heated to volatilize the GC-amenable compounds, which are then localized at the front of the relatively cold analytical column. (iv) The column then undergoes normal temperature programming to

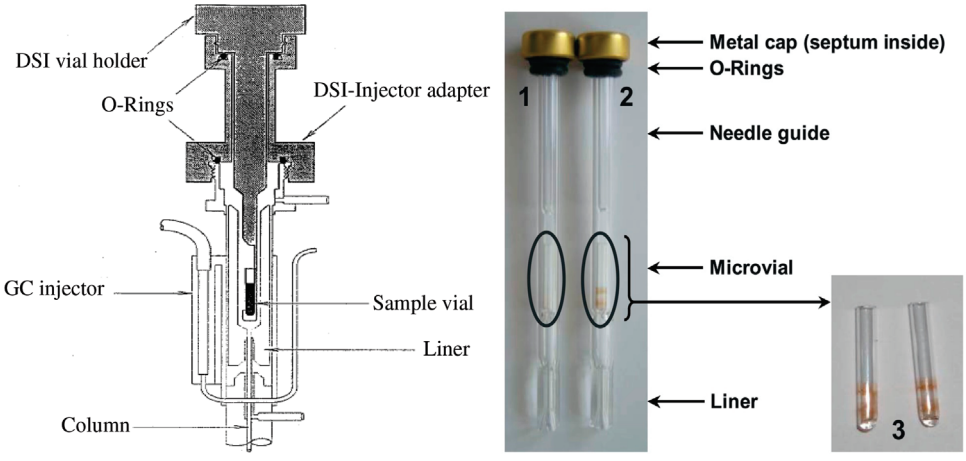

Figure 2.8 (a) Drawing of the ChromatoProbe used in DSI (reproduced with permission from Ref. [28]. Copyright 1997 IM Publications.) and (b) a DMI liner (reproduced with permission from Ref. [37]. Copyright Wiley-VCH Verlag GmbH.)

separate the analytes and cool to initial conditions. Afterwards, the microvial is removed and discarded along with the nonvolatile matrix components. Unlike liquid injection techniques with syringes, an elegant aspect of this sample introduction technique is that the volatility range of the compounds entering the GC liner and the column matches the volatility range of the GC system. In the commercial DMI approach, the entire liner, along with the microvial, is replaced after each injection. The main advantages of DMI are (i) reduced demands for GC system maintenance (contrary to other injection techniques, contamination by nonvolatile matrices does not occur), (ii) reduced effort in sample preparation (it is possible to eliminate the cleanup step), and (iii) shorter GC analysis time (through the increase in sample throughput) [35–37].

2.4 Comparison of Different Injectors

The on-column injection is a superior technique in terms of the nondiscriminative transfer of sample components into the GC system; however, it provides no separation of analytes from matrix coextracts. For "dirty" samples, for example, plant materials, vaporizing injection techniques are the most suitable. "Classical" hot splitless injection is the most frequently applied injection technique; however, some adverse effects, including discrimination of low volatiles, sorption, and thermodegradation can occur. Significant suppression of these effects in the injection port can be achieved by the application of pressure pulses during the splitless period (pulsed splitless injection) [38–43].

At present, the use of pulsed splitless injection for the analysis of organic contaminants has been often reported. This setup (an increase in column head pressure for a short time – usually 1 or 2 min – during sample injection) leads to an increased carrier gas flow rate through the injector (several times higher than normal) and in turn enhances the transport of sample vapor onto the GC column. Under these conditions, the residence time of the analytes in the injection chamber is much shorter than in classical splitless injection. In some cases, a significant suppression of analyte adsorption and/or degradation (but also discrimination) occurs in the inlet port. The responses obtained with pulsed splitless injection in the case of troublesome compounds are significantly higher than those obtained with common splitless injection. Due to the increased pressure, higher volumes of sample can be injected (up to 5 μl) without the risk of backflash and consequently lower detection limits can be achieved [41,43–47].

The problem closely connected with the injection port is matrix-induced chromatographic response enhancement ("matrix effects"), which provides unexpected high recovery compared to matrix-free solvent calibration. As the cause of matrix effects lies in the injection port, the injection technique can significantly influence their extent. The long-term stability and matrix effects of different injection methods have been compared. Three methods were compared: on-column pulsed splitless, PTV solvent split, and PTV splitless injections. It was found that the PTV solvent split injection was the most effective in reducing the matrix effect and this technique also has the best long-term stability. Therefore, the tolerance of the GC system to coinjected matrix components increases in the following order: on-column < pulsed splitless < PTV solvent split technique [48,49].

A comparison of frequently used injection techniques is presented in Table 2.1.

Table 2.1 Comparison of injection techniques.

Types	Injection volume (μl)	Sensitivity		Long term stability
		In general	Thermolabile compound	
Hot split	1–2	Low	Not good	Stable
Hot splitless	1–2	Moderate	Not good	Moderate
Pulse splitless	2–5	High	Good	Stable
On-column	2–3	High	Good	Not stable
PTV split	30	High	Good	Stable
PTV splitless	30	High	Good	Stable
SFSI	1 mg	High	Not observed	Stable

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