APPLICATION NOTE

Gas Chromatography

Key Features

- Reduced discrimination
- Compatibility with labile species
- Extended volatility range
- On-column injection capability

Large-Volume Injection Technique with the Programmable Split/Splitless Injector

The Programmable Split/Splitless Injector

The PerkinElmer Programmable Split/Splitless (PSS) injector is one of the most powerful and flexible capillary inlet systems currently available to gas chromatographers. It offers significant advantages relative to standard split/splitless (S/S) flash-vaporizing injector techniques.

Another advantage of the PSS is that it retains the beneficial "ease of use," concentration range flexibility and robustness of a conventional split/splitless injector. It has a removable liner to prevent column contamination and can be routinely applied to all samples for which a standard S/S injector is normally recommended.

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For the Better

Solvent Purging

These injection techniques extend the range of samples analyzed by GC while improving and simplifying the analysis of specific samples. One such technique, which is an enhancement to splitless injection, is called solvent purging and is illustrated in Figure 1 and described below.

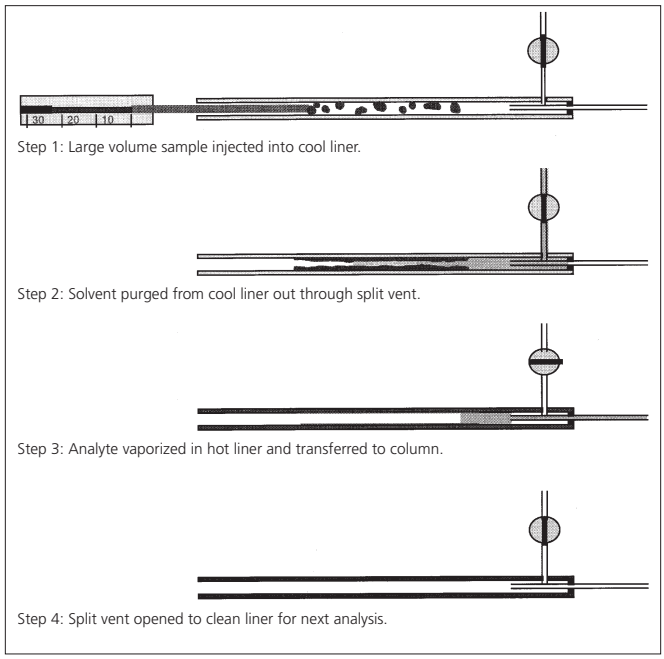

Figure 1. Operational sequence for solvent purging.

Operational steps in solvent purging:

1. The sample solution is injected into the PSS liner, which is held at a low temperature.
2. The solvent vapor is purged from the liner and out through the open split vent. Less volatile analytes will remain within the liner.
3. When all, or most, of the solvent has evaporated, the vent is closed and the temperature of the liner is raised to vaporize the analyte residues. These are then transferred, without splitting, into the chromatographic column where chromatography takes place.
4. The split vent may be reopened after a further delay to assist in the cleanup of the liner after each injection.

Benefits of Solvent Purging

Removing the solvent from the sample prior to entering the column offers several benefits to an analysis.

- The chromatographic solvent peak is much smaller, giving cleaner and faster chromatograms.
- The column inlet is not exposed to liquid solvent which may cause migration or swelling or other degradation of the stationary phase.
- Sensitive detection systems, such as mass spectrometers, are protected from potentially harmful amounts of solvent.
- Solvent flooding effects are eliminated, giving improved peak shapes and, hence, resolution.
- Nonvolatile material in the sample is prevented from entering the column, thus offering an extra level of protection to the column.
- Large volume injection becomes possible.

Figure 2 shows examples of chromatographic improvements made possible by applying a solvent purge technique to a low level solution of PCBs.

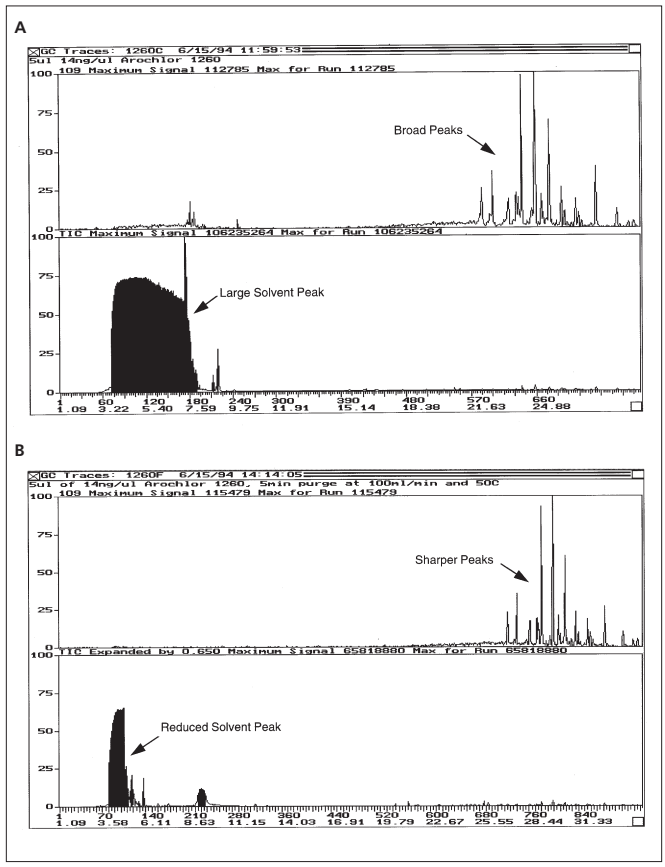

Figure 2. **A.)** Classical 5 µL splitless injection of 14 ng/µL Arochlors in iso-octane; **B.)** Same as **A** but with solvent purging.

Application of Solvent Purging

The only requirement of solvent purging is that the analytes of interest must remain within the liner as the solvent is being purged. This precolumn separation will only be achieved when either:

- The analytes are less volatile than the solvent, or
- The injection liner is packed with an adsorbent which preferentially retains the analytes.

Thus, solvent purging is best suited for samples with a highly volatile solvent and relatively nonvolatile analytes. It would be inappropriate to use this technique for volatile analytes in a less volatile solvent.

Large-Volume Injection

In the past the main obstacle to large-volume injection (LVI) has been the difficulty in removing a large amount of solvent from the system in an efficient, simple and rugged manner so that chromatographic performance is not compromised. There are various techniques that have been developed for this purpose but these often require specialized hardware and considerable skill on the part of the operator. Using the solvent purge technique described earlier, solvent removal becomes a fast and easy process. Standard GC hardware is used as listed below:

- PerkinElmer AutoSystem Gas Chromatograph
- PSS Injection System
- Standard AutoSystem autosampler (optional but recommended)
- 50 µL syringe
- Any capillary column
- Any detection system

The key to the success of LVI with the PSS injection system is the availability of a wide-bore (2 mm I.D.) injector liner as shown in Figure 3.

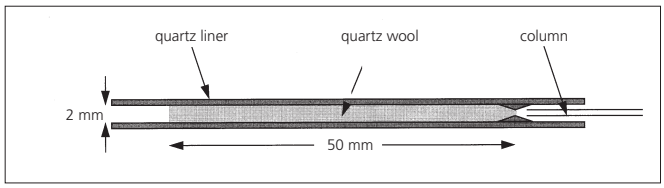

Figure 3. Wide-bore injector liner used with PSS for LVI.

The liner is tightly packed with quartz wool, which retains the large volume of liquid sample after injection. Figure 4 shows chromatography of a simple mixture of n-alkanes from different volume injections. It can be seen that this liner is able to accept injection volumes up to at least 100 µL without apparent degradation of the chromatography.

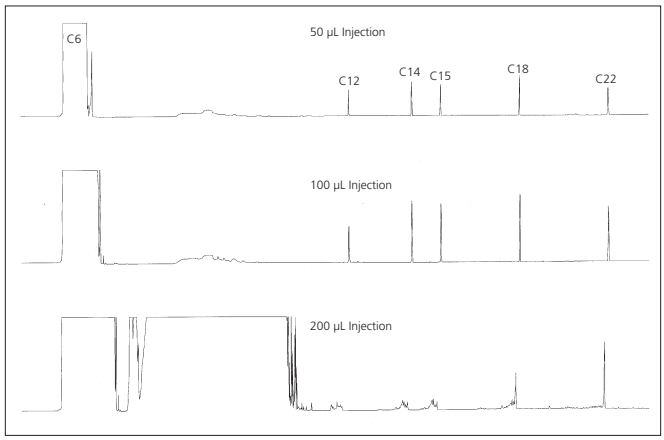

Figure 4. Capacity of the 2 mm PSS liner. 200 mL injection shows degradation of C12-C15. Sample: 0.3 ng/µL n-alkanes in hexane by manual injection. Five minute solvent purge at 50 °C and 100 mL/min.

If a narrow-bore liner of 1 mm internal diameter is used, the effective capacity of the liner is greatly reduced to about 10-20 µL. Larger volume injections are then only possible if the solvent is vaporized as it is being injected (*i.e.,* partial concurrent vaporization). This is possible but requires extreme care in setting up liner temperatures, gas flows and injection speeds (*i.e.,* a specialized autosampler may be required). The wide-bore liner is much more tolerant of the applied conditions and methods are much easier to develop and apply using standard hardware.

Because the hardware is standard it can be used, without modification or any compromise in performance, for other applications not requiring LVI (*i.e.,* for conventional 1 µL and <1 µL injection volumes). Table 1 lists the key operational modes possible, with and without an autosampler, with the hardware listed above.

Table 1. **Operating modes of the PSS system.**

Operating Mode	Manual Injection	Autosampler Injection
Cold On-Column	Yes	Yes
Programmed Split	Yes	Yes
Programmed Splitless	Yes	Yes
Programmed Splitless with Solvent Purge	Yes	Yes
Programmed Splitless with Solvent Purge and LVI	Yes	Yes

LVI Performance

Figure 5 shows the area precision from 100 autosampler injections of 50 µL of a solution of n-alkanes in hexane. These data not only demonstrate excellent quantitative performance but also the extreme ruggedness of the system in tolerating these huge volumes of solvent being injected.

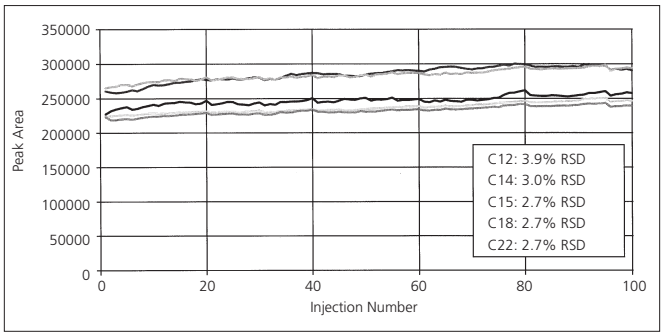

Figure 5. Quantitative precision using the PSS injection system for LVI: 50 µL injections of 0.3 ng/µL n-alkanes in hexane.

One obvious concern with LVI is the risk of carryover from injection to injection. Figure 6 shows an autosampler injection of a relatively strong solution of n-alkanes in hexane immediately followed by an injection of only the solvent. The results clearly show that not only does the solvent purge eliminate most of the solvent from the column but it also cleans up the system very effectively for the next analysis.

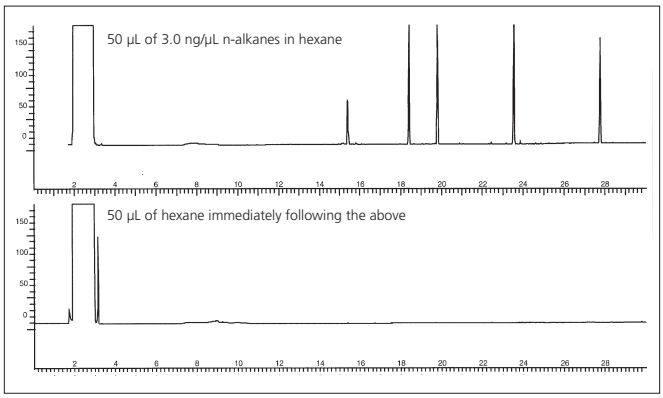

Figure 6. Chromatograms showing lack of carryover between successive analyses. Five-minute solvent purge at 50 °C and 100 mL/min.

Figure 7 shows how the absolute peak area varies as the autosampler injection volume is adjusted. Good linearity is observed across the range 5-50 µL.

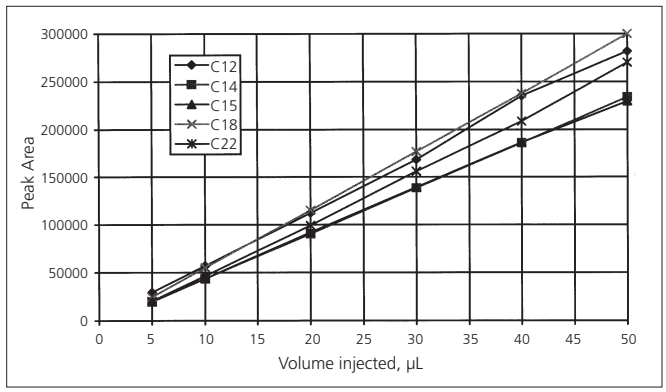

Figure 7. Effect of autosampler injection volume on peak area. Sample: 0.3 ng/µL n-alkanes in hexane.

As stated earlier, LVI using solvent purge is really only suitable for analytes less volatile than the solvent. Figure 8 shows the relative recovery for a range of n-alkanes under one set of conditions. The volatility cutoff (C12 in this case) will vary according to the applied conditions. Listed below are some of the measures that can be applied to extend the technique to more volatile analytes but, it should be remembered that techniques such as equilibrium headspace and purge and trap are usually better suited to this type of sample.

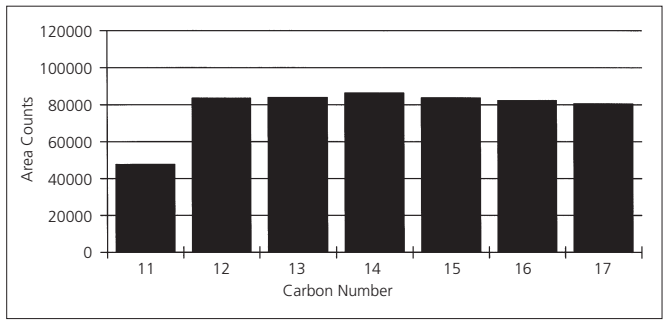

Figure 8. Volatility range of LVI using PSS iwht solvent purging. Sample: 0.14 ng/µL n-alkanes in hexane. Five-minute solvent purge at 50 °C and 100 mL/min.

Measures to extend LVI volatility range:

- Use a more volatile solvent.
- Cool the liner, using the PSS subambient accessory if necessary, to a lower temperature.
- Pack the liner with a suitable adsorbent material.

LVI Applications

Figures 9, 10, and 11 show some examples of applications for this technique.

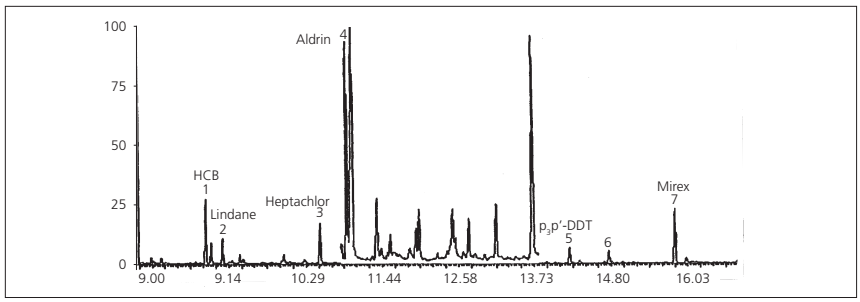

Figure 9. Total ion chromatogram from a 50 µL injection of a hexane extract of soil with organochlorine pesticides. Concentrations in extract: aldrin 23 ng/mL, mirex 12.5 ng/mL, others 5 ng/mL.

Column: 25 m x 0.25 mm i.d., 0.12 µm methyl silicone

Carrier Gas: Helium 195 kPa, split flow: 250 mL/min

PSS: liner: packed with Chromosorb®-750 coated with Dexsil™-300 30 °C (0.5 min); ballistically to 320 °C (10 min)

GC: 40 °C (1.5 min); 20 °C/min to 140 °C (0 min); 10 °C/min to 300 °C (1 min)

Events: Split valve initial: ON
0.5 min: OFF
5.5 min: ON

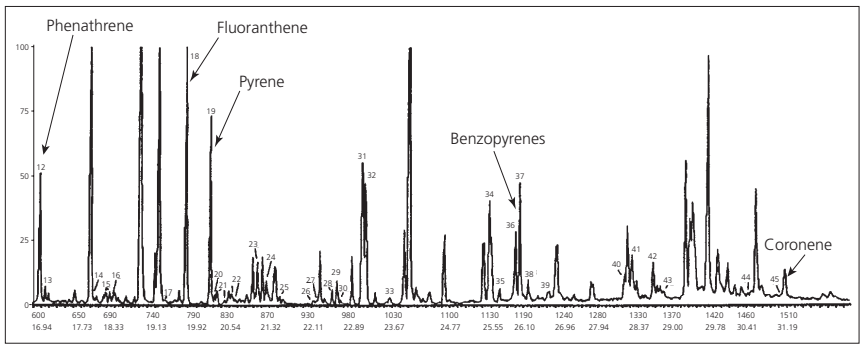

Figure 10. Total ion chromatogram from a 50 µL injection of a hexane extract of soil with polynuclear aromatic hydrocarbons at the low-ppb level.

Column: 25 m x 0.25 mm i.d., 0.12 µm methyl silicone

Carrier Gas: Helium 195 kPa, split flow: 250 mL/min

PSS: liner: packed with Chromosorb-750 coated with Dexsil-300 30 °C (0.5 min); ballistically to 340 °C (10 min)

GC: 40 °C (4.5 min); 10 °C/min to 300 °C (5 min)

Events: Split valve initial: ON
0.5 min: OFF
4.5 min: ON

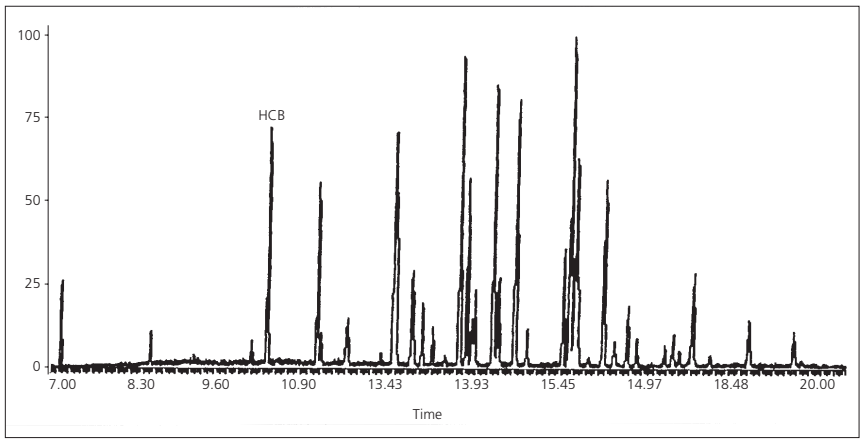

Figure 11. Total ion chromatogram from a 50 µL injection of a hexane extract of soil with polynuclear aromatic hydrocarbons at the low-ppb level.

Column: 25 m x 0.25 mm i.d., 0.12 µm methyl silicone

Carrier Gas: Helium 195 kPa, split flow: 250 mL/min

PSS: liner: packed with Chromosorb-750 coated with Dexsil-300 30 °C (0.5 min); ballistically to 340 °C (10 min)

GC: 40 °C (4.5 min); 10 °C/min to 300 °C (5 min)

Events: Split valve initial: ON
0.5 min: OFF
4.5 min: ON

Source: Technical University of Eindhoven, Netherlands.

Benefits Of Large-Volume Injection

As described in the introduction to this application note, the PerkinElmer programmable split/splitless (PSS) injector provides the most advanced available capillary column injection technology for conventional 0.5-5 µL injection volumes. The option of LVI is simply an additional feature of the standard PSS injector. The increased sensitivity it offers has wide application in clinical testing and in food/environmental analysis.

Sensitivity is a particularly critical issue in environmental monitoring applications such as the analysis of pesticides, PCBs and PAHs in water and soil. These routine environmental procedures benefit considerably from the enhanced detection limits of large-volume injection. Sample throughput and data quality are other key factors affecting productivity in the environmental laboratory.

By eliminating or minimizing the requirement for labor-intensive sample preconcentration before GC analysis, LVI reduces the risk of error introduction and significantly improves sample throughput.

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