Large-Volume Injection for Gas Chromatography Using COC-SVE

Application

Gas Chromatography

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Authors

Bill Wilson, Don Nixon, and Matthew S. Klee
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808-1610
USA

Abstract

Large-volume injection (LVI) is a valuable tool for trace analysis by gas chromatography (GC). New inlets and injection techniques have been developed in recent years that enable volumes up to 1 mL to be injected into a standard GC.

This application note describes LVI with a cool on-column (COC) inlet and solvent vapor exit (SVE) kit and is illustrated with examples of straight-chain hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and semivolatiles.

Key Words

Large-volume injection, LVI, solvent vapor exit, SVE, gas chromatography, GC, PAH analysis, hydrocarbon analysis, semivolatile analysis.

Introduction

The increasingly lower detection limits required by regulatory agencies have fueled a demand for more sensitive gas chromatography (GC) analysis. Large-volume injection (LVI) techniques are one response to this demand. Other approaches include sample concentration techniques, the use of more sensitive and selective detectors, and decreasing system noise. See "Large-Volume Injection for Gas Chromatography Using PTV" for a discussion of approaches to increase sensitivity.[1]

The typical injection volume for capillary column GC analysis is 0.5 to 2 µL. The Agilent 6890 and 5890 Series GCs allow approximately two times the normal injection volume (up to 5 µL, depending on the solvent) using "pulsed" splitless injection. Injecting still larger volumes by standard techniques can lead to contamination of the system, irreproducible results, and loss of sample. In LVI, good chromatography is obtained with injection volumes of 5 to 500 µL or more. While putting a large volume of sample into the column is an intuitive and conceptually simple approach, special techniques are required to remove the excess solvent. To be successful, LVI demands hardware modifications to remove the solvent and careful method development.

To inject large sample volumes, the bulk of the solvent in which the sample is dissolved must be selectively evaporated before transfer of the sample to the analytical column and the start of the analytical separation. There are two primary techniques to eliminate solvent: programmable temperature vaporization (PTV) and cool on-column (COC) injection with solvent vapor exit (SVE). LVI with PTV is recommended for samples with no early-eluting compounds of interest or for dirty samples. This is discussed elsewhere.

COC-SVE

LVI by COC injection and SVE uses a COC inlet to introduce the sample. A precolumn assembly, consisting of a retention gap/precolumn combination, is placed ahead of the analytical column. A vent line is attached at the juncture of the precolumn and analytical column as shown in figure 1.

Liquid sample is injected into the precolumn. The solvent evaporates and

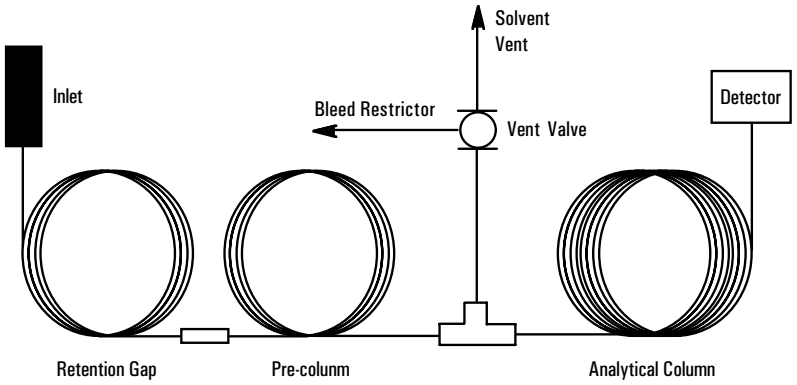

Figure 1. COC Injection with SVE—Hardware Configuration

exits through the vent. The oven temperature, column head pressure, and tower are set so there is always some liquid solvent in the precolumn. Sample components, including volatiles, are concentrated in this small volume of solvent. The time required to evaporate this solvent can be predicted with the software included in the COC-SVE kit. After evaporating the bulk of the solvent, the vent is closed and the normal oven temperature ramp is started. The remaining sample is then evaporated from the precolumn and moves to the analytical column for separation. This process allows solutes that elute very close to the tail of the solvent to be retained and analyzed.

An SVE kit is available with all the necessary columns, valves, fittings, and software (G2399A). The software in the COC-SVE kit simplifies method development. Enter the oven temperature, inlet pressure, outlet pressure, vent flow, and amount injected. When you select the solvent from the drop down list, the software automatically calculates the delay time. Figure 2 shows the COC-SVE top level screen.

The 6890 Series GC uses a standard automatic sampler fitted with up to 50-µL syringes to introduce LVI samples. Up to 25 µL can be injected with a single injection from the 50-µL syringe. The injection parameters are set in the Agilent ChemStation software.

With COC-SVE, there is an increased probability of contaminating the precolumns because such large volumes of sample are injected directly. Nonvolatile components remain in the precolumn and may influence subsequent injections. The precolumn may have to be cut or replaced frequently. COC-SVE is primarily used for clean samples such as drinking water extracts.

Table 1 lists the advantages and disadvantages of LVI by COC-SVE. See "Large-Volume Cool On-Column Injection using the G2399A Solvent Vapor Exit Kit" for further discussion and other examples of COC-SVE.[2]

Experimental

A 6890 GC with electronic pneumatics control (EPC) was used for these experiments. Samples were injected with the G1916A automatic liquid sampler (ALS) with a G1513A injector. A G1876AA ChemStation (version 4.02) was used for instrument control and data acquisition.

Table 2 shows the hardware and software revisions that support LVI with COC-SVE.

The SVE configuration described in the introduction is shown in figure 1. The experimental conditions for the GC methods are given with each chromatogram.

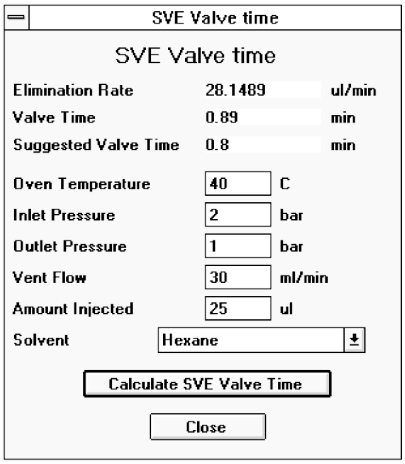

Figure 2. COC-SVE Software

Table 1. Advantages and Disadvantages of LVI with COC-SVE

Advantages	Disadvantages
Can be used with early-eluting compounds	Requires clean samples
Minimizes degradation of unstable components	Less flexible technique
Minimum sample discrimination	Complex to optimize for new solvents

Table 2. Software, Hardware, and Firmware Versions that Support LVI

Item	Software/Firmware
ChemStation software	A.04.02 or higher
G1513A injector	A.09.10
G1512A ALS controller	A.01.08
6890 Series GC	A.02.01 or higher

Results and Discussion

Fairly large sample volumes can be injected using COC injection without SVE, as shown in figure 3, as long as a retention gap is used.

Figure 3A shows the chromatogram obtained from 10 µL of a PAH sample without SVE, and figure 3B shows 20 µL of the same sample. Twice the volume of sample was injected for the chromatogram in 3B as in 3A and yielded a twofold response with no deterioration of peak shape (see table 3 for the method parameters for these experiments). The ability to inject such large volumes by COC requires use of a very non-polar solvent such as isooctane.

Figure 3C shows what happens if additional sample is injected and the retention gap overfill ed. Injecting smaller amounts of a polar solvent, such as methanol, would have a similar effect. Using COC-SVE allows the injection of such large samples without overfilling the retention gap.

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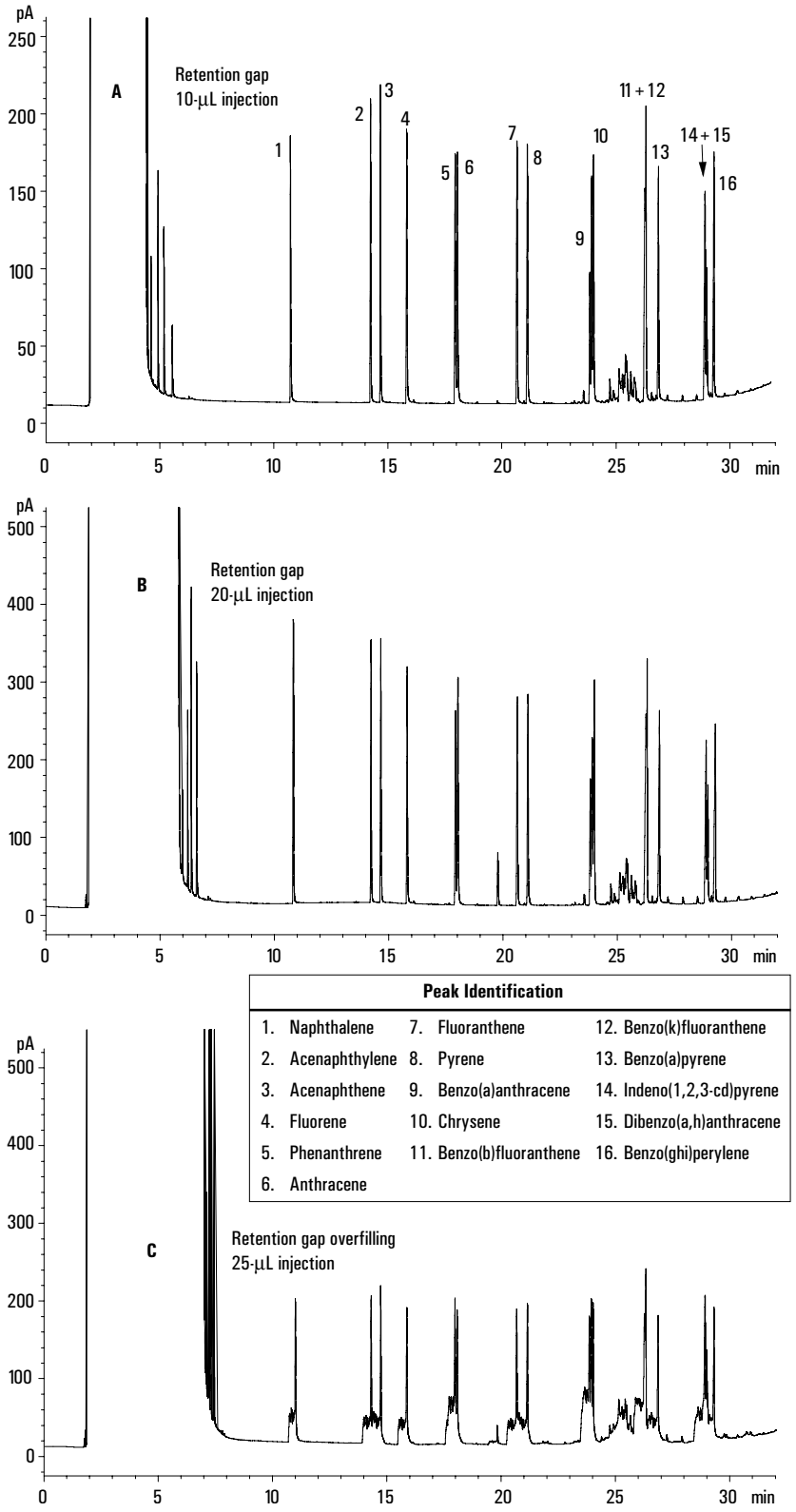

Figure 3. PAH Analysis by LV-COC injection without SVE peaks

Figure 4 shows a COC injection of 10 µL of a C_{10} to C_{14} mixture without SVE. The C_{10} is well separated from the solvent. To compare the recovery of LVI, 25-µL of a 1:25 dilution of the same sample using SVE is also shown. The area counts of the C_{10} and C_{12} peaks of the two chromatograms are similar. This demonstrates the value of large-volume injections of dilute samples, which yields proportionally lower detection limits.

Notice the pronounced solvent impurity peaks with the larger injections. This is a universal weakness of all LVI techniques and highlights the need for meticulous lab technique and ultra-clean solvents.

A valuable use of COC-SVE is in the analysis of semivolatiles in drinking water extracts. Figure 5A shows the chromatogram from an injection of 1-µL of an undiluted test solution using a standard method (SVE valve closed during whole run). The test solution was diluted 1:25 and reanalyzed using a 25-µL injection and a 0.45-minute solvent vent delay time (see table 4 for other analytical parameters). The chromatogram is shown in figure 5B. By comparing figures 5A and 5B, it is clear that no chromatographic resolution is lost and that the peak heights for each solute are very similar.

Table 3. PAH Analysis by LVI by COC Injection Without SVE Conditions for Figure 3A, 3B, and 3C

Item	Without SVE
Inlet type	Cool on-column
Injection volume	Dichloromethane, 10, 20, or 25 µL
Injection speed	Slow, 3 sec postdwell time
Column	30 m x 0.25 mm id x 0.24 µm HP-5 MS
Retention gap	5 m x 0.53 mm id
Oven temperature program	50 °C, 5 min; 10 °C/min to 320 °C
Carrier	1.5 mL/min hydrogen; 1.6 CF 66 kPa initial P

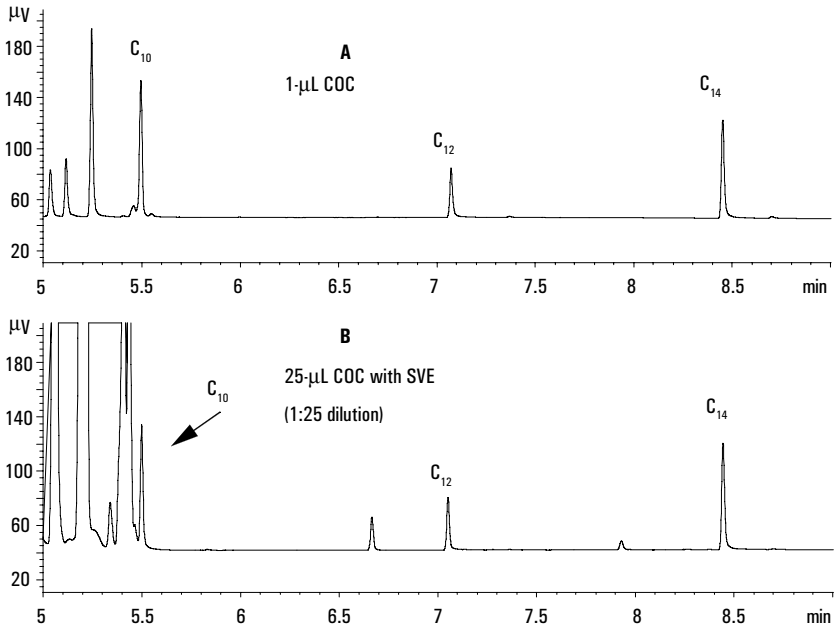

Figure 4. C_{10} to C_{14} in hexane by COC injection—comparison of 1-µL standard and 25-µL LVI injections

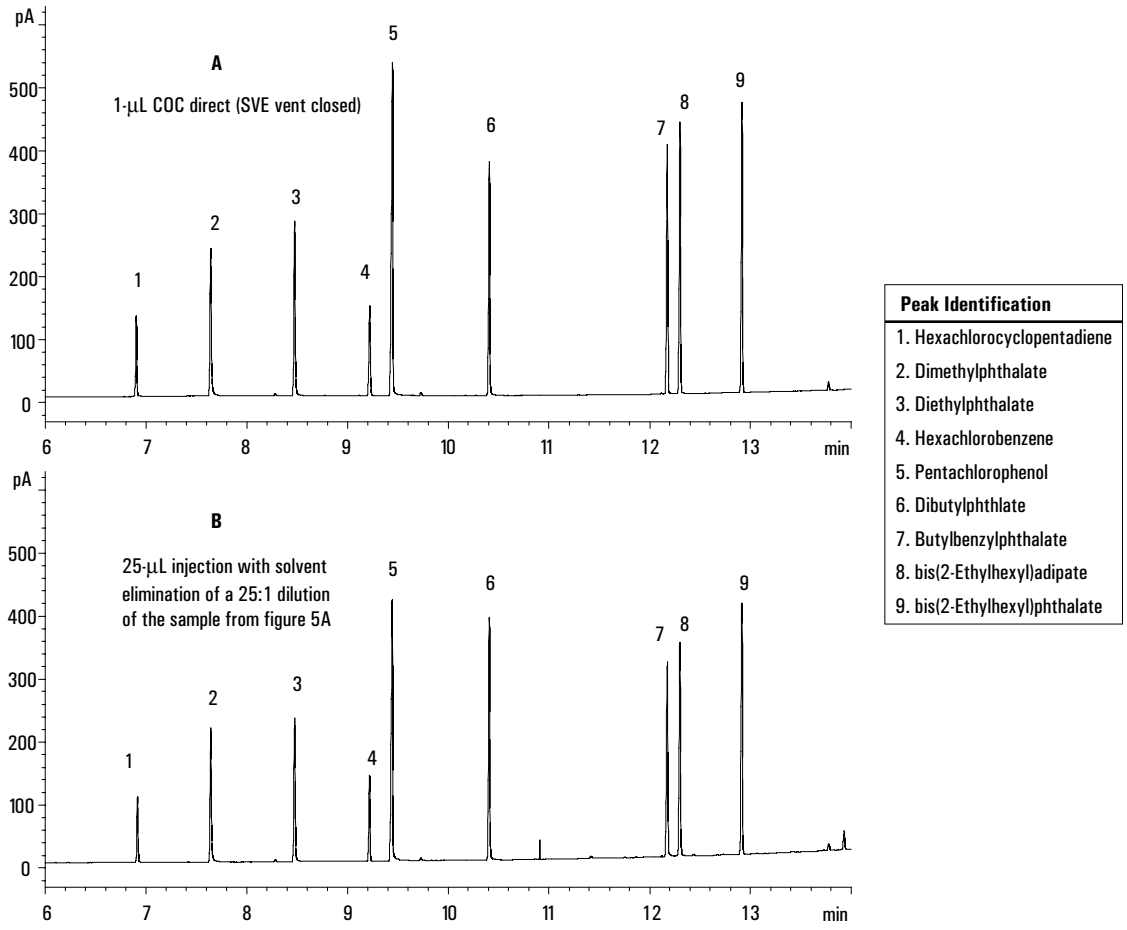

Figure 5. COC-SVE of an extract of semivolatiles in drinking water—for conditions, see table 3

Table 4. Conditions for Figure 5

Sample	Semivolatiles
Solvent	Acetone
Solute concentration	4 ppm
Parameter	
Injection	Cool on-column
Inlet temperature	Oven track
Injection volume	25 µL
Carrier gas	Hydrogen
Column flow	2 mL/min
Oven temperature 320 °C, (2 min)	45 °C (1 min), 20 °C/min to
SVE on time	0 minute
SVE off time	0.45 minute
Detector	FID
Detector temperature	320 °C

Conclusions

LVI is a useful technique for lowering detection limits for GC analysis. LVI with COC-SVE is ideal for clean samples with early-eluting compounds. With careful method development, it is a reliable technique with broad applicability for sample applications that require more sensitivity than can be obtained with standard injection volumes. The COC-SVE kit provides the hardware and software necessary to be successful with performing the SVE technique.

References

1. M. S. Klee, et al, "Large-Volume Injection for Gas Chromatography Using PTV," Agilent Technologies, Inc., Application Note 228-374, Publication (23) 5965-7770E, March 1997.

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