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Gas Chromatography/Mass Spectrometry | APEX ProSep™

The APEX ProSep™ 800 XT Plus Precolumn Separation Inlet: Advantages of a Chromatographic Zone as GC Inlet System

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Introduction

In typical GC or GC/MS analyses, only a fraction of the injected components is of analytical interest; the remainder are interferences or of no interest (e.g., injection solvent). Eliminating these unnecessary components provides substantial improvements, such as increased analytical integrity and less frequent maintenance. However, there are few technologies available that offer selectivity *in situ;* usually extensive bench chemistry has been the rule. A recent advance in injection-port technology, the APEX ProSep™, provides several approaches to selecting which components are introduced onto the GC column.

The ProSep inlet design functions as an independent chromatographic zone and provides some preselection prior to compound introduction onto the analytical column. ProSep exploits this preseparation and can selectively reduce or eliminate certain injected components without compromising the components that are of analytical interest. The solvent of a large-volume injection (LVI), for example. Similarly, high-boiling compounds that are associated with sample matrix and are not of analytical interest can be vented, thereby avoiding contamination of sensitive detectors such as mass spectrometers. It is this ability to perform chromatographic separation that differentiates ProSep from strictly thermal-desorption or programmed-temperature-vaporization inlet devices.

This note presents a generalized demonstration of selected ProSep capabilities. Using a simple mixture, we demonstrate the selective elimination of solvent from a large-volume injection, a late-eluting or high-boiling interference, and a compound of intermediate elution.

ProSep™ Function

The ProSep Precolumn Separation Inlet system consists of four components:

1. Preseparation Column Module
2. Electronics Control Module
3. Flow Control Module
4. Preseparation Column

The Electronics and Flow Control modules control the temperature and flow settings of the Preseparation Column module. The Preseparation Column is a glass or silica precolumn that fits inside the Preseparation module similar to a split/splitless glass liner, but it is 24 cm in length. ProSep function is diagrammed in Figure 1. At injection, ProSep sets the GC in split mode. Because ProSep provides some separation, injected components are organized in the precolumn according to boiling point. Solvent, analyte, and matrix become ordered in the port, and the low boiling solvent is rapidly vented through the open split vent (Step 2). After solvent elimination, the temperature of the Preseparation Column Module is ramped and the split vent closed, transferring analytes into the analytical column (Step 3). After the last analyte of interest is transferred, the split vent is again opened and the Preseparation Column Module temperature ramped to bake off detrimental matrix components (Step 4). Software controls all aspects of the preseparation module condition.

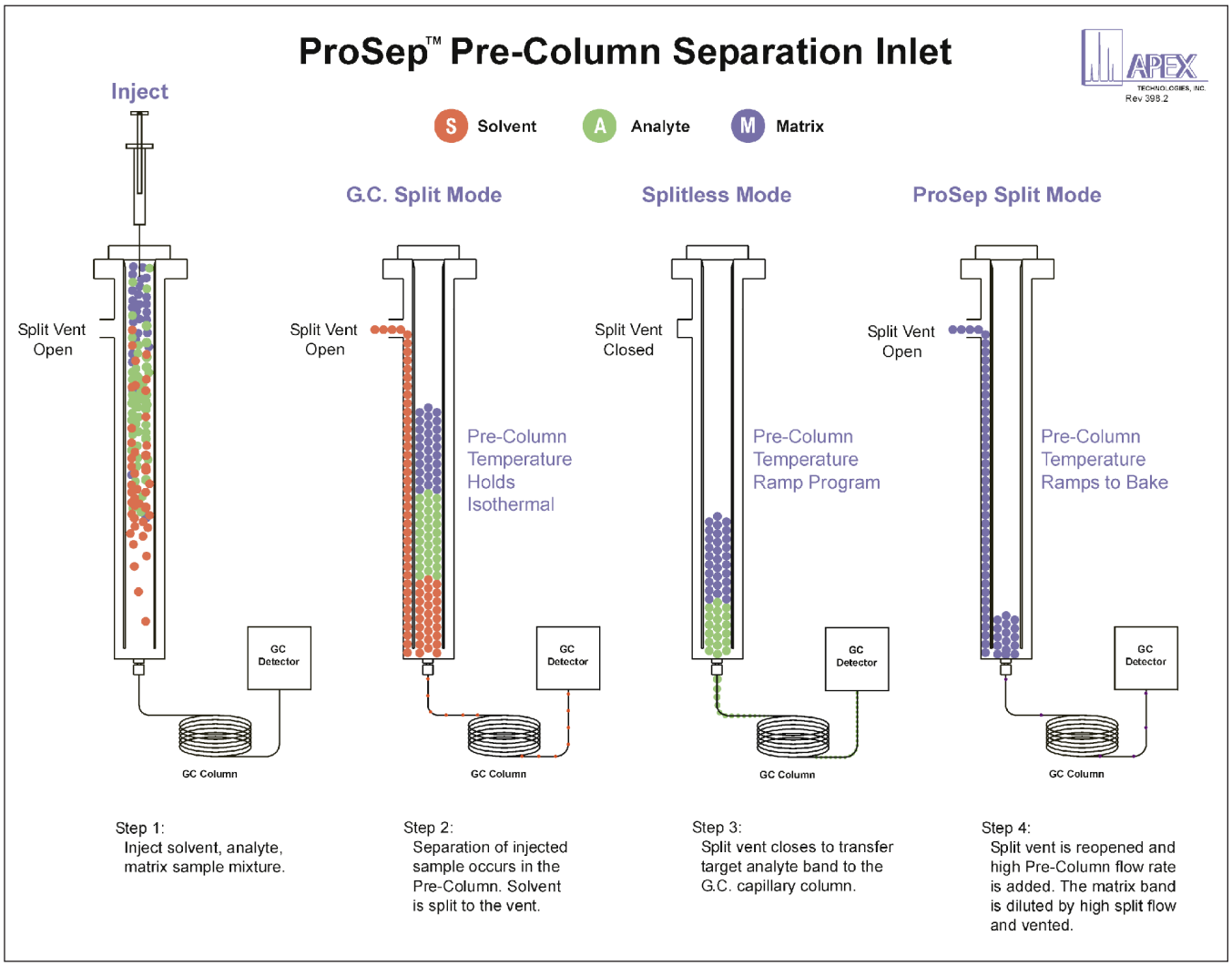

Figure 1. ProSep function.

Experimental

The APEX ProSep™ 800 XT Plus Preseparation Column Module portion of Precolumn Separation Inlet [PSI] system, Figure 2, was installed in one of the two available injection ports of the Agilent Technologies 6890 Plus Gas Chromatograph (GC). The other port was a split/splitless port. The appropriate gas and electronic connections were made to the Flow and Electronics Control Module and software was installed for control of the ProSep system. The 6890 GC and Agilent Technologies 5973 MSD were controlled by the standard software (G1701BA). All injections were made by the integrated 7683 automatic liquid sampler with either 10-µl or 50-µl syringes as appropriate to the 1-µl or 10-µl injection volumes. A 30-m, 0.25-mm i.d., 0.25-µm film HP-5MS column was used as the analytical column. The Preseparation Column was phase coated with HT-5, and contained HT-5 coated fibers and a plug of silica wool in the upper 4–7 cm of the column. The 5973 MSD was operated in full scan mode (56–280 amu). The instrumental arrangement is shown in Figure 3.

The four-component mixture consisted of dodecane, biphenyl, 4-chlorobiphenyl and methyl palmitate in hexane (made by 1:10 dilution of Part number 05970-60045 in hexane). Before applying LVI, a small-volume 1-µl injection of the four-component mixture in hexane solvent was made to establish relative abundances of the compounds. The ProSep Preseparation Column Module was held isothermal at 275°C to elute all components and was maintained in the splitless mode to transfer all analytes to the GC column.

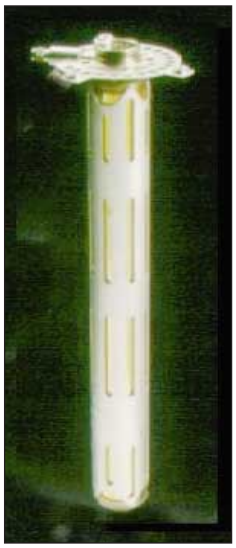

Figure 2. ProSep Preseparation Column Module.

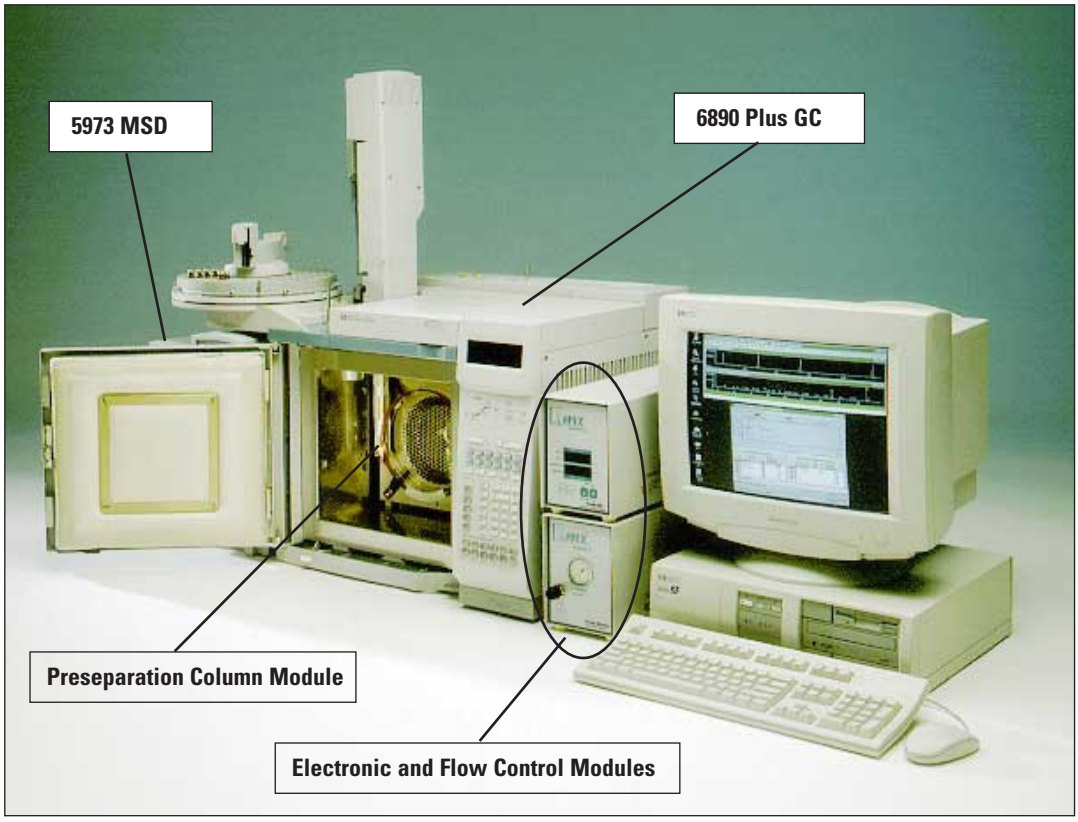

Figure 3. Instrument Configuration.

LVI Experiments

Next, ProSep was used to scale from 1-µl to 10-µl injections. (ProSep allows for injection volumes up to 125-µl). The Preseparation Column temperature was set at 80°C at injection (*above* the 69°C boiling point of the hexane), and the split mode was held for about 6 sec to vent the hexane. By optimizing these ProSep parameters, a nearly tenfold increase in signal was obtained (Figure 4). (The high value for the MS threshold holds the gain just under a factor of ten). Because this 10-µl injection takes place at essentially the same speed as the 1-µL injection, the separation of the hexane, a C_6 hydrocarbon, from dodecane, a C_{12} hydrocarbon, is rapid.

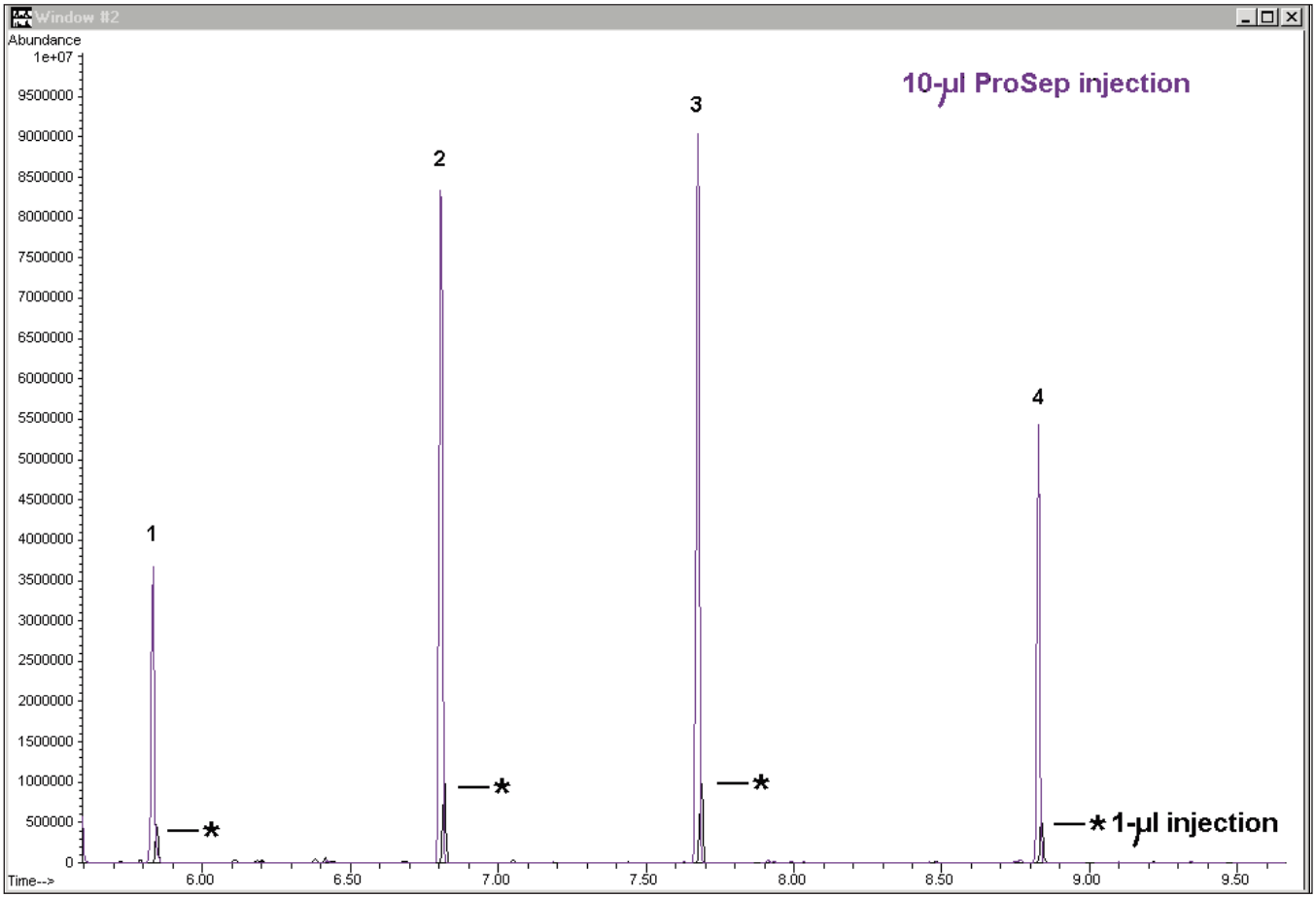

Figure 4. ProSep-GC-MSD total ion chromatograms of 1-µL and 10-µL injections of the four-component mixture in hexane. In order of elution, the compounds are dodecane, biphenyl, 4-chlorobiphenyl, and methyl palmitate. The pattern of components in LVI closely matches that in SVI but the compound abundance is nearly tenfold higher.

Selective Reduction of Components

Consider the first peak in Figure 4, which is the dodecane component, an uninteresting impurity, perhaps a solvent-related contaminant. By delaying the transition to splitless mode, ProSep can selectively attenuate just this first peak (Figure 5). Although this is still a 10-µL injection, dodecane has been attenuated 20-fold, reduced to less than it was in the initial 1-µL injection. Selectively removing dodecane implies separating dodecane (boiling point 216°C) from biphenyl (boiling point 255°C) in the precolumn.

Suppose the last eluting peak, methyl palmitate (the fourth peak in Figure 4 and Figure 5), to be a high boiling, matrix-related contaminant that can adversely effect detector performance or degrade the column. By returning to split mode later in the Precolumn Separation Inlet program, ProSep can reduce the amount of this component that is introduced. Figure 6 shows a reduction in this component by approximately 50-fold, which is of the order of the GC split ratio.

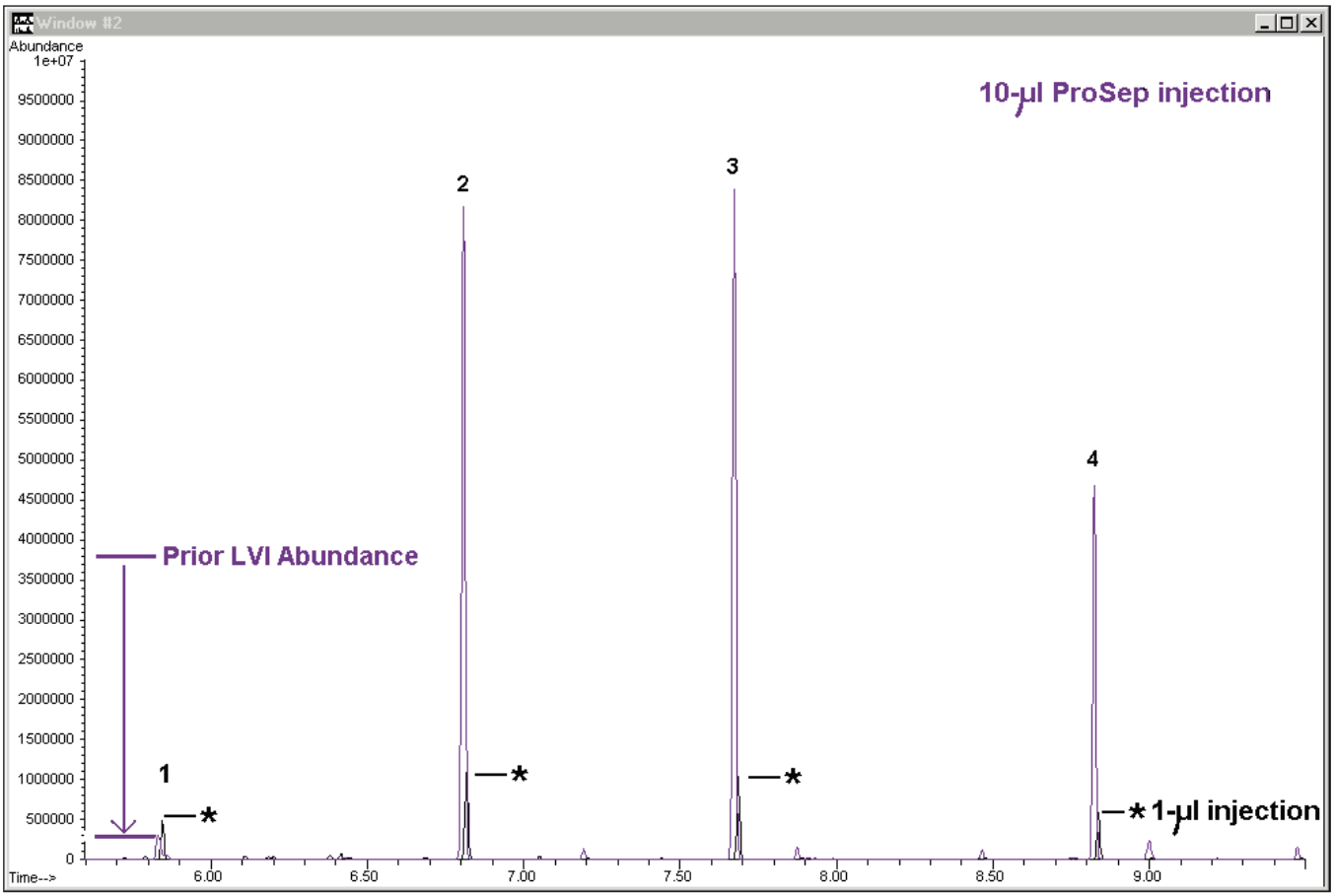

Figure 5. ProSep-GC-MSD total ion chromatograms of 1-µL and 10-µL injections of the four-component mixture in hexane showing selective reduction of the first component, dodecane, without affecting the other components. This represents selective discrimination against dodecane (b.p. 216°C) without affecting biphenyl abundance (b.p. 255°C), the second peak, or remaining analytes.

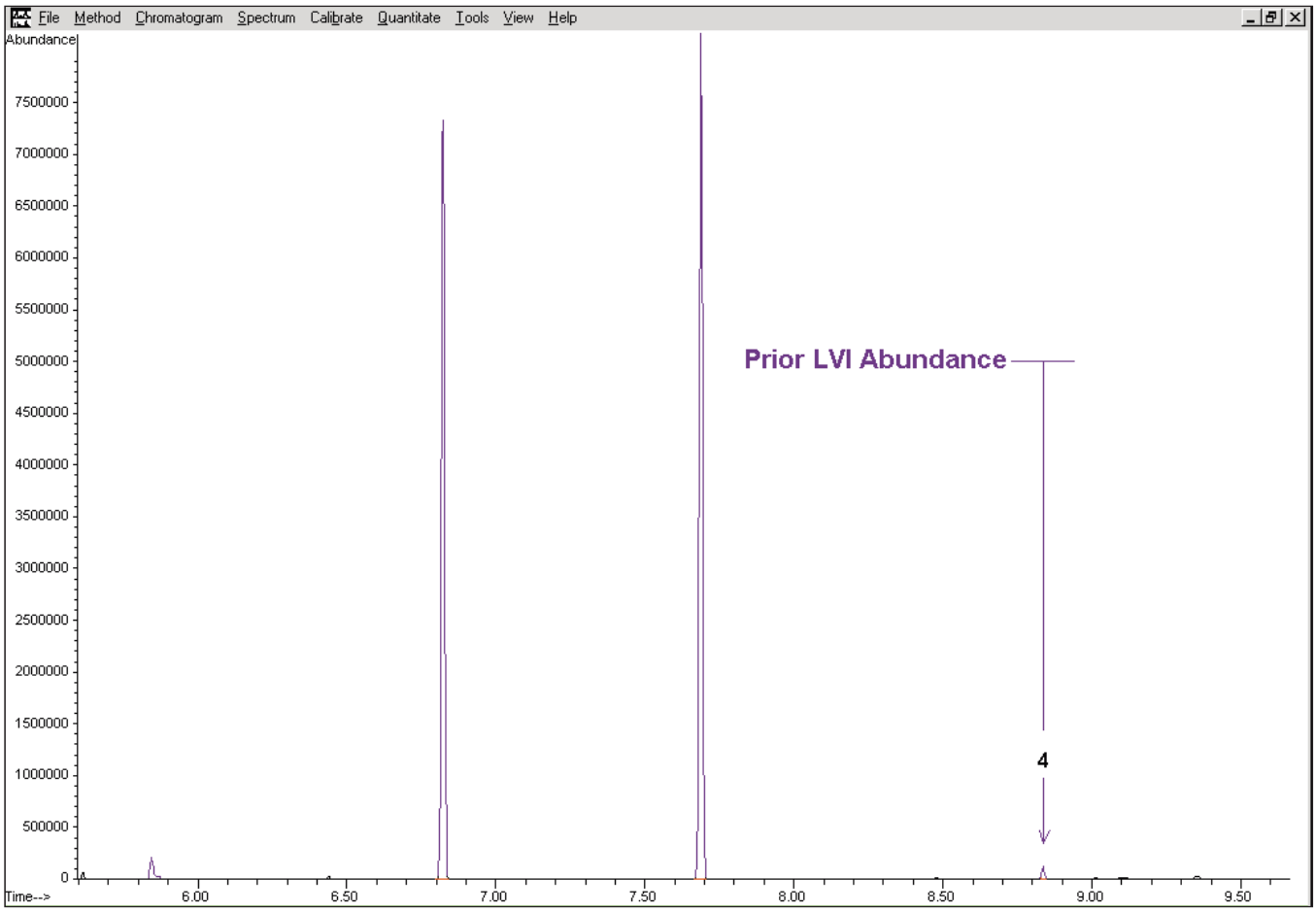

Figure 6. Selective reduction of a late eluting "matrix interference." ProSep-GC-MSD total ion chromatograms of 10-µL injection of the four-component mixture in hexane showing selective reduction of the last component, methyl palmitate, without effecting the other components by returning to the "GC Split" mode later in the Preseparation Column Module program. Reduction is of the order of the split ratio, here a factor of approximately 50.

ProSep can also apply additional purge gas to the preseparation column in a mode known as "ProSep™ Split." Essentially, this mode implements very high split ratios, e.g., ratios >1:250. Consequently, very high reductions of matrix contaminants are possible. Applying "ProSep Split" mode to the methyl palmitate reduces its response below the threshold (Figure 7). Combining this mode with a high Preseparation Column Module temperature flushes matrix contaminants from the preseparation column and prevents matrix accumulation during LVI.

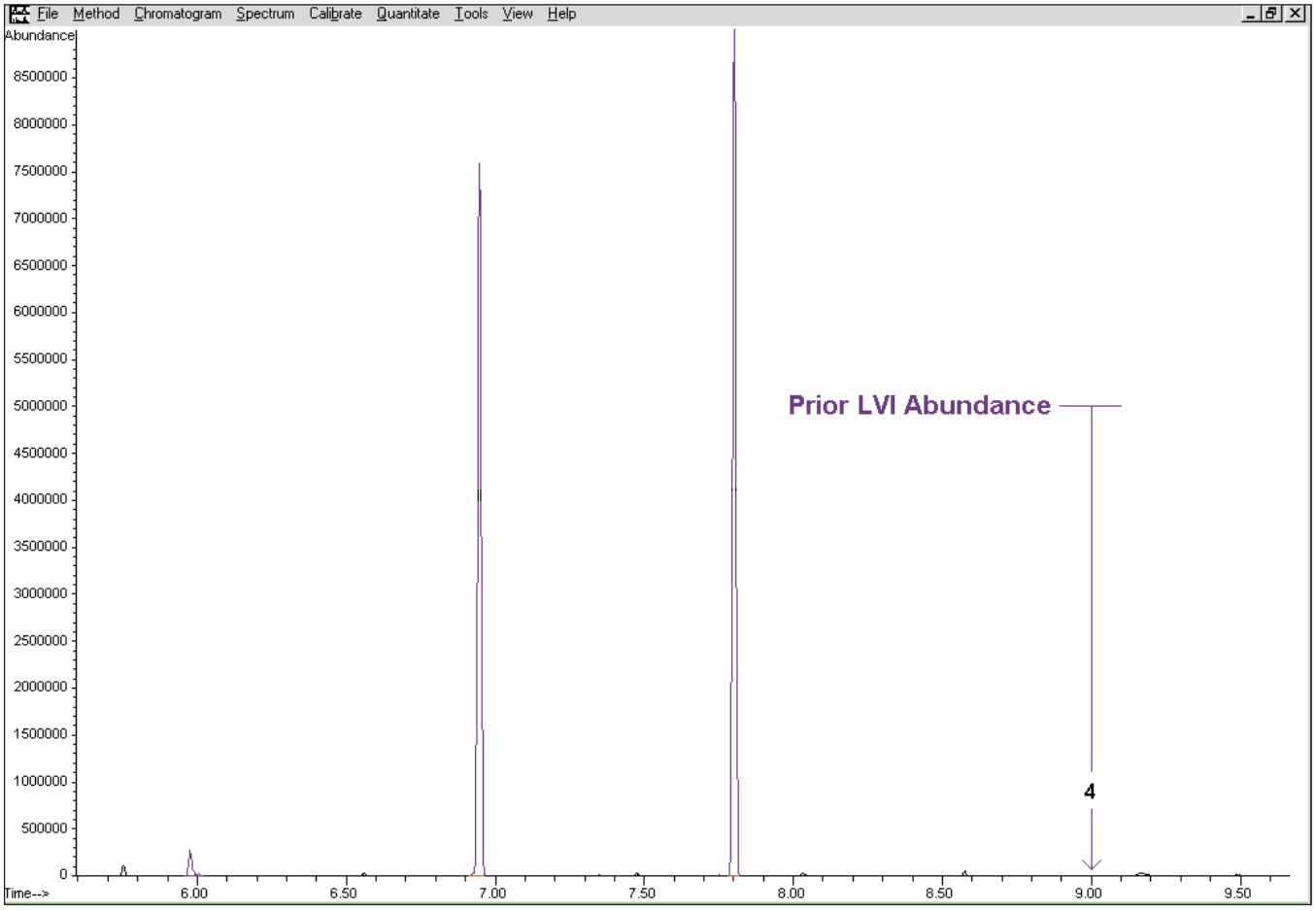

Figure 7. Application of "ProSep Split" mode to eliminate high boiling "matrix interference." ProSep-GC-MSD total ion chromatograms of 10-µL injection of the four-component mixture in hexane showing selective reduction of the last component, methyl palmitate, without effecting the other components by applying "ProSep Split" mode later in the Precolumn Separation Inlet program. Reduction from the previous abundance is of the order of approximately 1/250.

Conclusions

The data illustrate the capability of the APEX ProSep Precolumn Separation Inlet device to make separations in the LVI mode and to function as a chromatographic zone. If there were no separating power, selectively removing components would not be possible; for example, separating dodecane from biphenyl. In this operating mode, the ProSep functions more like a packed column GC and so provides a crude GC-GC cleanup of the injected sample. Other features and techniques of selectively introducing compounds onto the analytical column are also available with ProSep; they will be described in forthcoming application notes and briefs.

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Work with authentic samples and a wide variety of matrices has shown the ProSep to be very reproducible and robust. Because injection and separation are rapid, sample throughput is very high. A wide variety of LVI applications can easily be developed from existing SVI methods based on this scheme. The data here were excerpted from training materials which guide the user in the development of their own LVI applications.[1]

Reference

1. Prest, H., O'Neil, G., and Hollis, J., APEX ProSep™ 800 Series Precolumn Separation Inlet Tutorial Revision 1.01. 1999: Apex Technologies, Inc., Cincinnati, Ohio, *www.Apex-Technet.com*

**Printed in the U.S.A. December 1999
(23) 5968-5747E**