HIGH-SPEED GAS CHROMATORGRAHIC ANALYSIS USING A TANDEM COLUMN ENSEMBLE AND STOP-FLOW MODULATION

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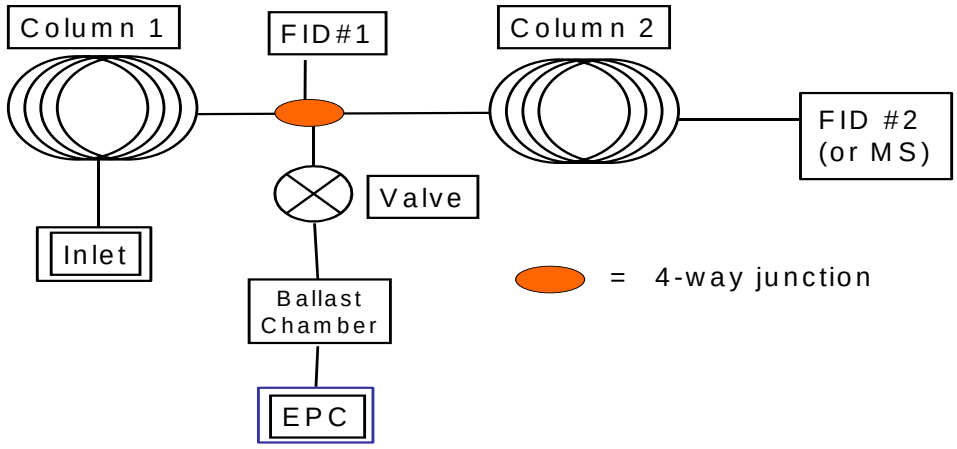
Most gas chromatographers are constantly challenged to improve analysis times without sacrificing separation. Additionally, most stationary phases used for GC separations do not exhibit the necessary selectivity to separate all compounds in most target compound lists. It is sometimes possible to find specially-designed columns for certain methods that allow for complete separation in reasonable run times, but most often chromatographers have to compromise the compound separation in order to get shorter run times. This is still a factor when using high-speed heating techniques, for the stationary phase selectivity is often the same as used in conventional GC separations.

While finding a single stationary phase with adequate selectivity to separate all of the target compounds in a reasonable time is often impossible, it is usually possible to find a combination of two dissimilar stationary phases that each have specific favorable selectivity for some of the target compounds. For example, if an analyst needed to separate both hydrocarbons and alcohols, the combination of a polydimethylsiloxane (or non-polar column like an Rtx-1) coupled with a polyethylene glycol (or polar column like an Rtx-Wax) may have, in combination, the necessary selectivity to resolve all compounds. This may require two independent analyses, using conventional instrumentation, for the sake of this example.

A powerful technique for separating complex mixtures, developed by Sacks, et. al.[1,2] at the University of Michigan, uses pressure-tunable selectivity and a series-coupled column ensemble. In this technique (termed: Stop-Flow GC), two standard-dimension capillary columns with dissimilar stationary phases are connected in series, using a 4-way junction. At this junction point, a source of carrier gas also is connected, with the pressure controlled by an external Electronic Pressure Control (EPC) unit, as shown in figure 1. An external valve controls the flow of the carrier gas to the junction point. A detector is connected to the fourth port of the junction, and monitors the components as they elute from the first column.

Figure 1. Diagram of the Stop-Flow GC system, originally described by Sacks, et. al.[1,2]



When an injection is made, the sample components move through the first and second columns. There are 4 possible scenarios for closely-eluting compounds A and B:
(1) A and B are resolved after passing through both columns
(2) A and B are not resolved after the first column, but are resolved after the second column
(3) A and B are resolved after the first column, but not after the second column
(4) A and B are not resolved after either column

For condition 1, the column ensemble meets separation goals, and no flow modification is necessary. For condition 2, the selectivity of the second column allows for compound separation, and again no flow modification is necessary. For condition 3, the first column met the separation requirements, but the second column causes a coelution. By applying a short (ca. 1 to 10 second) flow pulse at the junction point, it is possible to maintain separation of the compounds at the end of the column ensemble. This is where the stop-flow system is used to its fullest potential. Finally for condition 4, no flow modification will help the separation, and it would be necessary to choose another stationary phase for one or both of the columns.

Figure 2 depicts how this system would be used for the complete separation of 4 compounds using the stop-flow system. In this simplified case, all four compounds are separated by column 1, but coelute at the end of the column ensemble (Fig. 2a). This would be an example of case 3, as described in the above text. These are the compounds that benefit from the stop flow system. As compound A crosses the junction between the two columns at 28 seconds, the valve is opened applying inlet pressure to the junction point. This stops the flow in the first column, and increases the flow rate in the second column, moving compound A slightly faster, and retarding compound B which is still near the end of the first column. This causes the peaks to remain separated once the valve is closed (normal operation) and compound B crosses the junction. At this point the other two compounds C and D still coelute as they were also still in the first column when the valve was opened (Fig 2b). By applying another stop-flow pulse at 43 seconds, it is possible to split compounds C and D (Fig 2c), just as A and B were separated by the first pulse. Through a combination of column selection, and stop-flow pulsing, separations can be dramatically enhanced using conventional GC instrumentation.

Figure 2. Stop-Flow GC for optimizing the separation of coeluting compounds: (a) no stop-flow pulses; (b) pulse at 28s; (c) pulses at 28s & 43s.

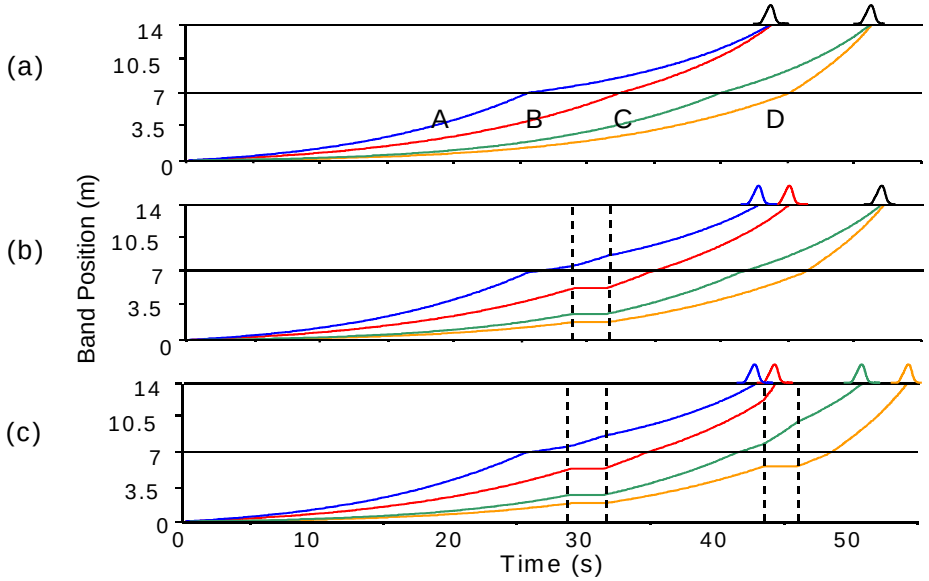
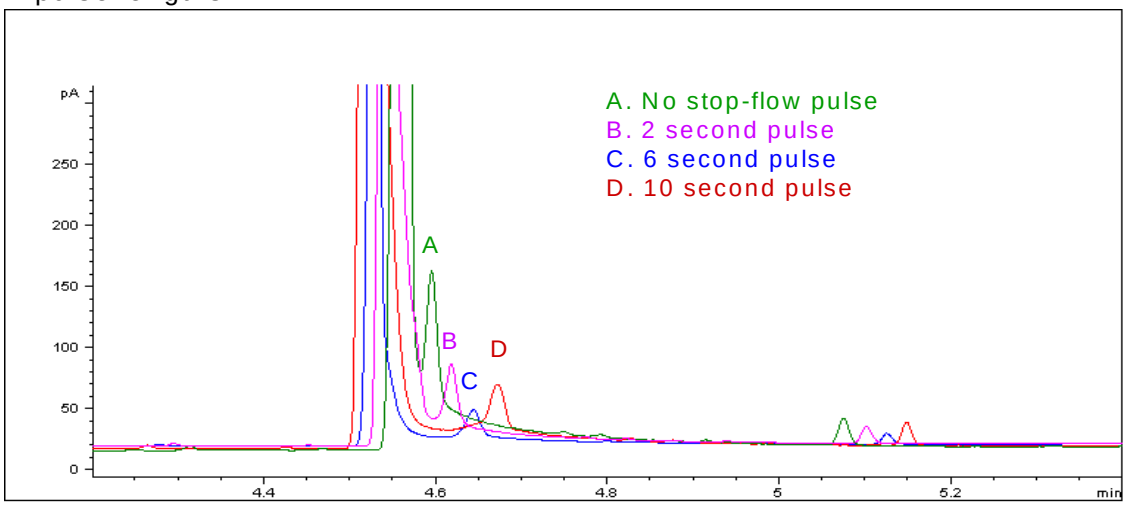


Figure courtesy of R. Sacks, University of Michigan

This system has been used for the separation of essential oils[3-6], chlorinated pesticides[7], and organic volatile impurities (OVI's)[8]. In all of these cases, complete separation was obtained with time savings of 50 to 80 % over the conventional GC separation that had coelutions in most cases.

This system can also be used to increase the separation between a large, or solvent-like peak, and a smaller trace component. Figure 3 are the various stop-flow chromatograms obtained for the separation of limonene and eucalyptol for an essential oil standard where limonene is the predominant component. In this case, it was desired to increase the time between these two compounds so the quantitation for the trace component was not compromised. By adding progressively longer stop-flow pulses (ca. 2,6and 10 seconds) it was possible to "push" the smaller eucalyptol peak away from the limonene peak, and thereby increasing the separation, without interfering with any of the other components in this analysis.

Figure 3. Separation of limonene and eucalyptol with increasing stop-flow pulse lengths.



CONCLUSIONS

Stop-Flow GC is an alternative to more expensive methods of improving analysis time, and in most cases allows for improvements in separation. By choosing two dissimilar columns that exhibit the necessary selectivity for the target compound list, it is possible to improve separation, and analysis time for many separations and still use conventional columns and instrumentation. The authors believe that this simple modification can allow most analysts to achieve significant improvements in their separation and sample throughput needs, and operation of this system is relatively simple. By improving the separation of closely eluting peaks using the stop-flow approach, and decreasing the "empty space" between many other peaks by increased oven temperature ramps, most laboratories can improve existing separations without the need to purchase expensive high-speed instrumentation.

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