

Introducing Stop-Flow GC, for High-Speed/High-Resolution GC Analysis

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Restek
Innovation

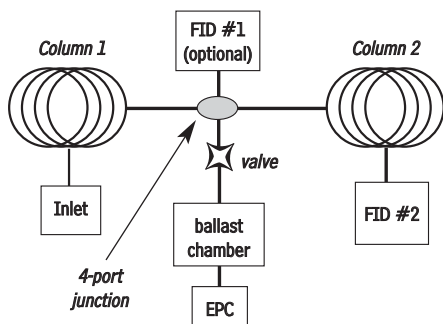
Developed in cooperation with investigators at the University of Michigan.

- ✓ Reduce analysis time by up to 70% while gaining resolution in difficult separations.
- ✓ Easy 30-minute installation.
- ✓ Complete system available from Restek.

Introduction

Analysis time is very important in GC applications but, often, shortening analysis time can sacrifice resolution. A powerful technique for separating difficult mixtures, developed by Dr. Richard Sachs and his colleagues at the University of Michigan, can greatly accelerate an analysis while maintaining—or improving—peak resolution. Stop-flow gas chromatography is performed by carefully timing interruptions to carrier gas flow at the junction of two series-coupled capillary columns that have differing selectivity for the target compounds in the analysis.¹⁻⁴ A low dead-volume valve (Figure 1), connected to a source of carrier gas at or above the GC inlet pressure, is used to program the flow through the column ensemble:⁵ by opening the valve, carrier gas flow is stopped or slightly reversed in the first column, but continues at the same rate, or at an accelerated rate, in the second column.

Figure 1 Schematic of a stop-flow GC system.



When using two GC columns in series (typically a non-polar stationary phase and a polar phase), there are four chromatographic possibilities for two closely-eluting analytes:

- 1) The compounds are resolved by the first column, and remain resolved at the outlet of the second column.
- 2) The compounds coelute on the first column, but are resolved on the second column.

In either case, the separation can be allowed to proceed without interference.

- 3) The compounds coelute on both the first column and on the second column.

In this case, other stationary phase combinations should be investigated to find a pair that separates the compounds.

- 4) The compounds are resolved by the first column, but coelute at the outlet of the second column.

In this case, the compounds can be kept separated if the valve is opened briefly (gas flow in the first column is stopped) when the leading compound in the pair has passed the junction, but while the trailing compound is still on the first column. The duration of the flow pulse is adjusted to ensure that the two compounds remain separated at the outlet of the second column.

Table 1 Commonly analyzed chlorinated pesticides used to illustrate stop-flow separations.

1. aldrin	11. dieldrin
2. α -BHC	12. endosulfan I
3. β -BHC	13. endosulfan II
4. δ -BHC	14. endosulfan sulfate
5. γ -BHC (lindane)	15. endrin
6. α -chlordane	16. endrin aldehyde
7. γ -chlordane	17. endrin ketone
8. 4,4'-DDD	18. heptachlor
9. 4,4'-DDE	19. heptachlor epoxide
10. 4,4'-DDT	20. methoxychlor

Example Application:

Analysis of Chlorinated Pesticides

By using series-coupled capillary columns, stop-flow pulses, and fast oven temperature programming, analysis times of less than four minutes are possible for the 20 commonly analyzed chlorinated pesticides listed in Table 1 (cat.# 32291).

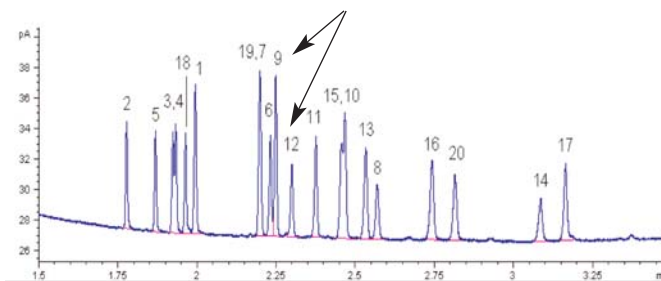
In this example, the column ensemble consisted of two 10m x 0.18mm ID columns. Column 1 incorporated a 0.20 μ m trifluoropropylmethyl polysiloxane bonded (polar) stationary phase, Rtx®-200. Column 2 had a 0.18 μ m 5% phenyl / 95% dimethyl polysiloxane bonded (non-polar) stationary phase, Rtx®-5. The columns were joined at a four-port junction, as shown in Figure 1. A flame ionization detector (FID) also was connected to the column junction, using deactivated fused silica tubing. Approximately 10% of the effluent was diverted to this detector, to monitor the analytes as they eluted from the first column. Flow interruption was provided by an external source of carrier gas, through a low-dead-volume valve connected to the crosspiece, as depicted in Figure 1. The valve was opened to slightly reverse carrier gas flow in the first column

Figure 2 Analysis of 20 chlorinated pesticides, using a polar column / nonpolar column ensemble.

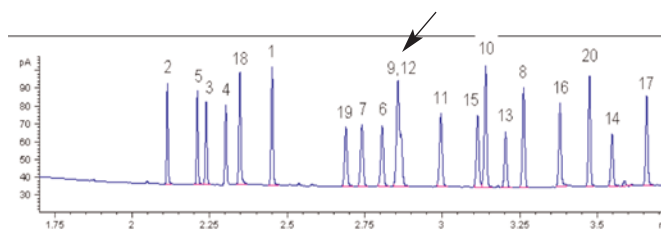
(a) FID chromatogram from column 1.

(b) FID chromatogram at the outlet of the column ensemble, no stop-flow pulse applied.

Conditions—Sample: 20-component chlorinated pesticide mix (cat.#32291, components listed in Table 1), diluted 1:20 in hexane to 10 μ g/mL each component; **GC Inlet Pressure:** 45.0 psig; **Inlet Temp.:** 300°C; **Oven Temp.:** 60°C (0.4 min. hold) to 220°C at 100°C/min., to 235°C at 15°C/min., to 300°C at 120°C/min. (0.5 min. hold) (total time 4 min.); **Injection:** splitless, 0.2–0.5 μ L, 0.25 min. splitless hold, 75mL/min. splitless purge flow, 2mm ID splitless injection liner (cat.#20712); **Detection:** dual FIDs, 300°C, 40mL/min. hydrogen flow, 400mL/min. air flow, 40mL/min. helium (make-up) flow, data collection rate set at 100Hz for both detectors.



a) Peaks 9 and 12 separated by the first column.



b) Peaks 9 and 12 coelute at the outlet of the second column.

(pressure at the junction point was set at 59 psig, 14 psig above the inlet pressure, causing a slight reverse flow on the first column while the valve was open). Ballast chamber pressure is controlled by an electronic pressure controller. The majority of the effluent was sent to the second FID to record the separation profile from the column ensemble.

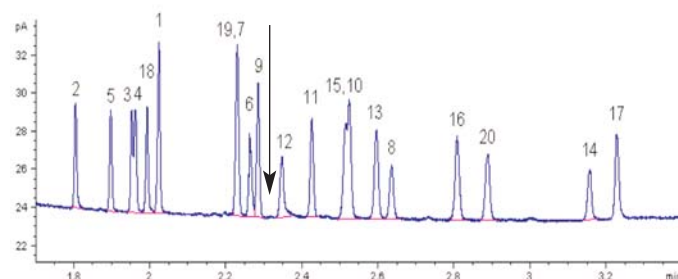
We analyzed the pesticides mix in the splitless mode, using the parameters described. Note that the inlet pressure and the temperature ramp are much higher/steeper than typical for this analysis. In order

for the stop-flow technique to enhance the separation of a critical pair, the component bands must be completely separated by the first column in the ensemble. One peak pair in the sample, 4,4'-DDE and endosulfan I, was resolved at the column junction (Figure 2a), but was not adequately resolved by the column ensemble (Figure 2b); we used a stop-flow pulse to improve this separation. Typically, the valve is opened for up to 10 seconds for each targeted component pair. In this study, we used a 5-second pulse.

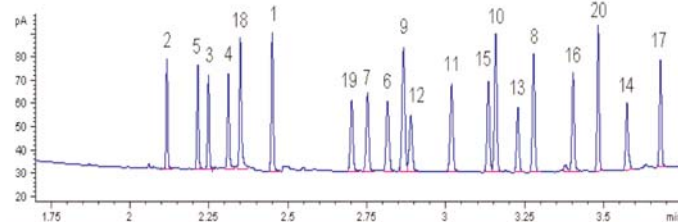
Figure 3a shows the signal from the FID monitoring the effluent from the first column, with an arrow indicating the time of the stop-flow pulse. When a 5-second pulse was applied beginning 136 seconds after injection, the 4,4'-DDE band had passed onto the second column, but the endosulfan I band had not reached the junction. Consequently, endosulfan I was retained on the first column during the pulse, while 4,4'-DDE continued to move along the second column. Figure 3b, the chromatogram at the outlet of the column ensemble (produced by the second FID), shows 4,4'-DDE and endosulfan I were resolved. Figure 3c is an enlarged view of the 4,4'-DDE and endosulfan I peaks with and without the stop-flow pulse. With the stop-flow pulse, the 20 chlorinated pesticides were resolved in less than 4 minutes.

Figure 3 Stop-flow GC enhances separation of 4,4'-DDE and endosulfan I, while reducing analysis time by 70%.

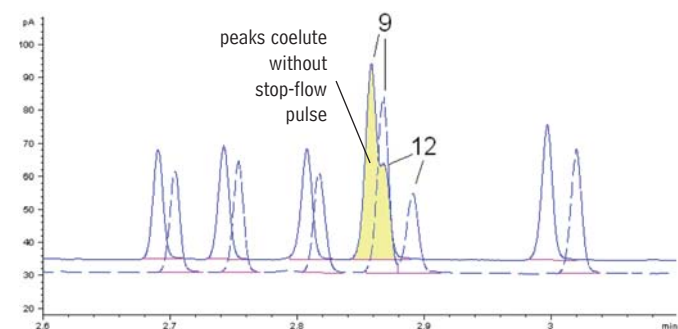
- (a) FID chromatogram from Column 1; arrow indicates initiation of stop-flow pulse.
 (b) FID chromatogram at the outlet of the column ensemble, one stop-flow pulse applied as shown in 3a.
 (c) Separation of 4,4'-DDE and endosulfan I, with and without the stop-flow pulse.
 Conditions: See Figure 2.



a) Chromatogram from first column, used to determine timing of stop-flow pulse.



b) Stop-flow pulse maintains separation of peaks 9 and 12.



c) Peaks 9 and 12 with and without stop-flow pulse.

--- with stop-flow
 — without stop-flow

This relatively simple use of the stop-flow system shows the tremendous potential of the technique—in this example, we reduced analysis time by approximately 70% (13 min. to 4 min.). Additional information is available in reference 6. Stop-flow GC, in combination with well-chosen column stationary phases, can dramatically improve many separations.

To find out how stop-flow GC can speed your analysis and improve problematic separations, contact us at support@restekcorp.com. We'll be happy to discuss column combinations and other particulars with you.

References

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Stop-Flow system easily attaches to your Agilent 6890 GC.

Stop-Flow GC Kit for Agilent 6890 GCs

Description	qty.	cat.#
Stop-Flow System for use with Cool On-Column EPC (includes: Stop-Flow enclosure, top mounting plate, 1-line weldment, and interface cable)	kit	21168
Stop-Flow System for use with Split/Splitless EPC (includes: Stop-Flow enclosure, top mounting plate, 2-line weldment, and interface cable)	kit	21169