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Capillary Flow Technology for Gas Chromatography: Reinvigorating a Mature Analytical Discipline

Capillary Flow Technology for Gas Chromatography: Reinvigorating a Mature Analytical Discipline

Bruce D. Quimby, James D. McCurry, and Wesley M. Norman,

Agilent Technologies, Inc.

In the half-century since its introduction, gas chromatography (GC) has evolved into one of the most widely used tools for chemical analysis. In the early years, packed columns were used for all applications, and several techniques were developed to extend the capabilities of the GC. Many of these were based upon connections made in the oven. Splitting to multiple detectors, heart cutting, and backflushing are examples of these techniques (1). In later years, when the majority of GC applications switched to higher performance capillary columns, techniques requiring in-oven column connections became much more challenging to implement. Success in achieving the required performance for capillary column connection devices was limited at best.

A new family of in-oven devices for capillary column connections has been introduced recently, based upon the capillary flow technique. These devices combine several new capabilities to meet the strict requirements of modern capillary chromatography. The ability to again routinely use techniques like splitting to multiple detectors (2), heart cutting (3–5), and backflushing (6) expands the usefulness of capillary GC, just as it did for packed column GC. Capillary flow also can be used to simplify new techniques like GC×GC. This article provides an overview of capillary flow and some examples of its application.

Optimizing Capillary GC Performance

For in-oven devices to be useful on a routine basis, they need to meet several requirements. They must be leak free, tolerant of high temperatures, reliable, and easy to use. They also must provide a low dead volume, a fast thermal response, and minimal outgassing into the sample path. The need for high temperature tolerance (400 °C) requires that the body of the device

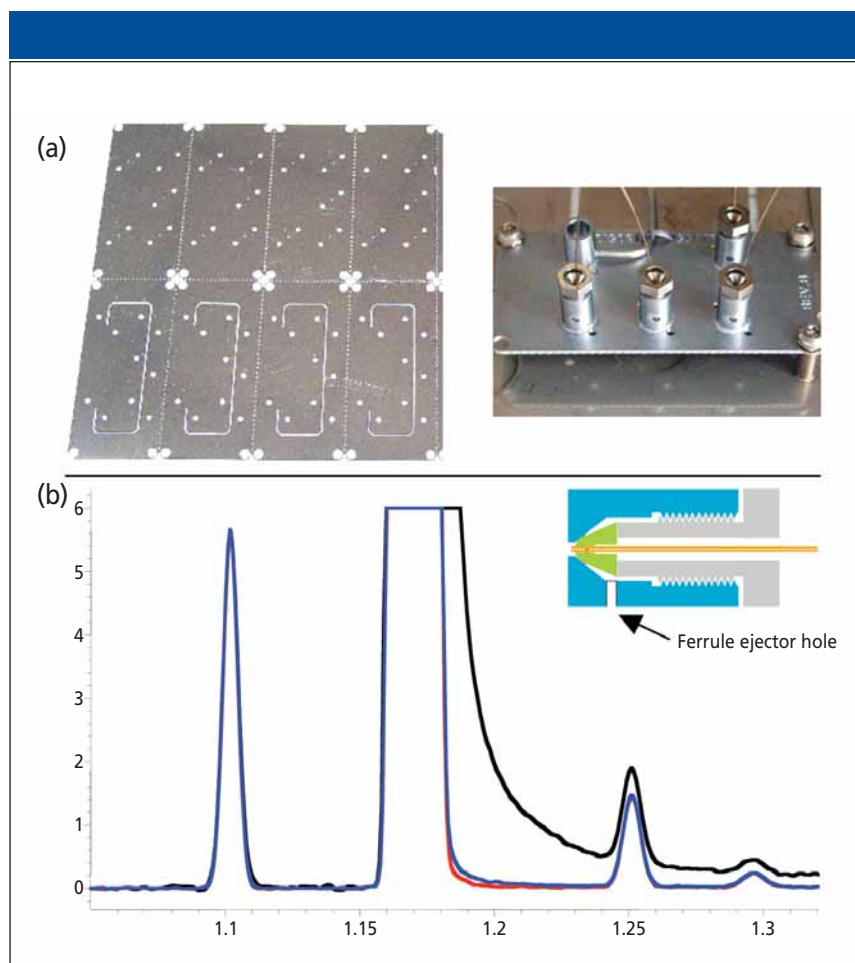


Figure 1: Principal components of capillary flow architecture: (a) Flow channels and through holes are etched into plates of a special grade of polished stainless steel. The two plate halves are folded, heated to more than 1000 °C under high pressure to produce a diffusion bonded flow plate, which is then chemically treated. (b) Overlay of hydrocarbon test mixture chromatograms run with the end of the column connected directly to the FID (black trace), through a polyimide-lined ferrule (blue), and through a metal ferrule (red). The well-swept void volume of the metal ferrule (inset) introduces negligible tailing.

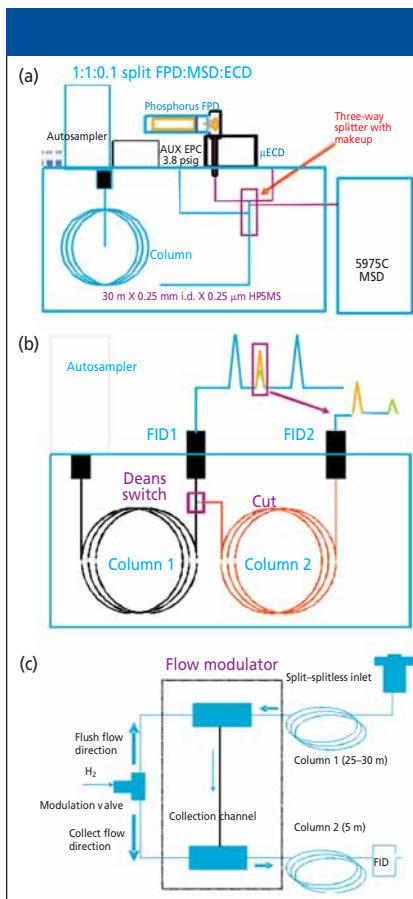


Figure 2: Capillary flow technology flow switching devices: (top) Three-way splitter with makeup gas collects chromatograms from two GC detectors and the mass spectrometer, (middle) Deans switch directs column effluent to one of two ports, and (bottom) flow modulator provides comprehensive, high resolution GC × GC without cryofocusing. All of these components support backflushing.

and the ferrules be made of metal. To meet the inertness requirement, the metal needs to be deactivated. One significant challenge is making the body of the devices with both a low thermal mass and low dead volume internal pathways.

The conventional approach is to machine the devices from solid blocks of stainless steel. While this works well for simple devices like unions, complex structures like Deans switches (3) and three-way splitters with makeup are much more challenging. The need here is for low dead volume and requires drilled holes of small diameters (typically 0.25 mm). These small holes can only be machined accu-

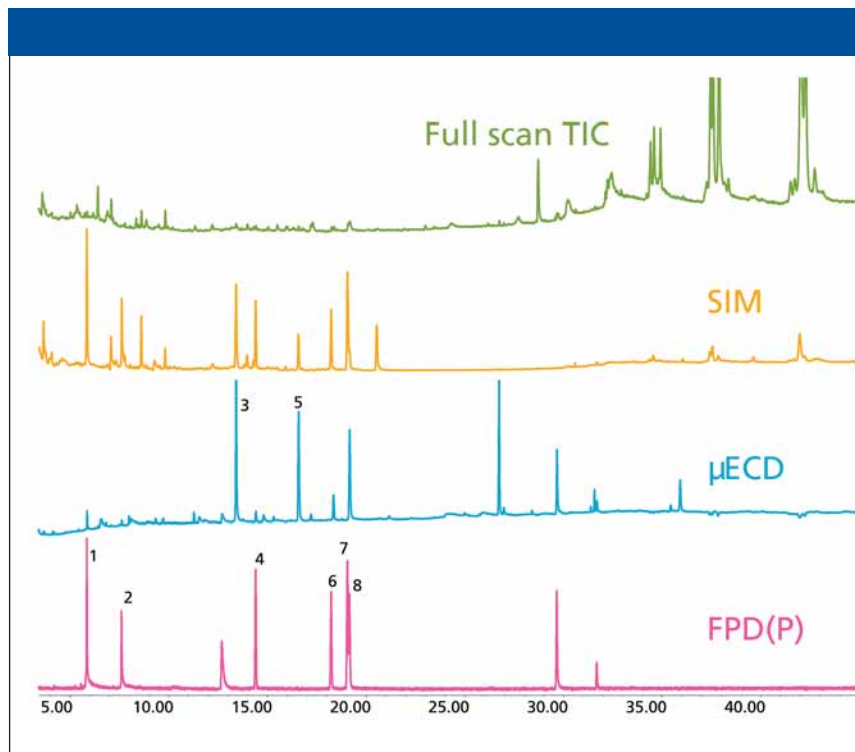


Figure 3: Determination of pesticides in milk. The three way splitter with makeup gas enables the collection of four individual signal trains in a single run. The μECD highlights electrophores such as polyhalogenated compounds, the FPD shows any phosphorus-containing compounds, and the MS SIM capability is used to search for a limited number of target compounds at very low levels. The full scan data are assessed with deconvolution reporting software (Agilent Technologies). Peaks: 1 = dichlorvos, 2 = mevinphos, 3 = β-BHC, 4 = diazinon, 5 = vinclozolin, 6 = pirimiphos-methyl, 7 = fenthion, 8 = chorpyrifos.

rately for short distances, thus, making the construction of manifolds very costly if even possible. This approach also results in significant thermal mass.

Capillary flow has overcome these obstacles by developing a new way of fabricating complex structures. Combined with several other improvements, this allows construction of in-oven devices that can be used routinely to solve difficult application problems. When implemented on the Agilent 7890A (Wilmington Delaware) gas chromatograph, these devices bring an enhanced suite of capabilities to modern GC applications.

Two of the major innovations that have enabled the development of capillary flow are the diffusion-bonded manifold plate and the metal ferrule connector. The plates are the basis for low-mass, low-dead volume devices that enable diversion and splitting of

gas flows to create a number of previously difficult capillary GC flow configurations. This flow architecture is formed in a manner similar to the manufacture of integrated circuits. Using photolithographic techniques, miniature features are etched onto one or both of a pair of plates that are bonded together to form a metallic sandwich containing the desired arrangement of internal flow channels (Figure 1a). The ability to create these channels and to make external flow connections to them over very small distances within the GC oven dramatically reduces dead volume. The low thermal mass of the integrated plate devices makes for efficient heat transfer that might otherwise result in a cold spot in the sample path. The plates themselves are formed from a special grade of stainless steel. After assembly, the interior surfaces in the sample path are coated with a deactivation layer.

Metal ferrules are used to provide leak-free connections and replace graphite ferrules or those with polyimide fittings. The graphite connectors are problematic because they have a tendency to shed particles while the polyimide fittings can become leak prone after repeated temperature cycling. The absence of a liner and the reduction in the annular space between the column and the metal ferrule reduces the tendency to trap solvents that can cause tailing (Figure 1b). The metal ferrule has a much lower tendency than the polyimide connector to become stuck in the fitting, and if it does, it is equipped with an ejector hole that simplifies its extraction.

Precision manipulation of gas flows is essential in modern capillary GC and even more so for the operation of capillary flow components. To better accommodate the needs of capillary flow devices, capillary GC systems have been equipped with both inlet and auxiliary (Aux) electronic pneumatic control (EPC) modules. The inlet EPC drives the chromatographic flow, while the Aux EPC provides a second flow system to introduce and control makeup gas for active diversion or splitting of the gas stream or for reversing flows for the purpose of backflushing the system. Calculators are provided that are able to compute the required flow and temperature parameters as well as the dimensions of restrictor tubing for each configuration. These calculators eliminate tedious computations and allow accurate prediction of flows and pressures before installation of a device. Controllers for GCs that support capillary flow technology devices also incorporate software designed to simplify the configuration and setup of methods.

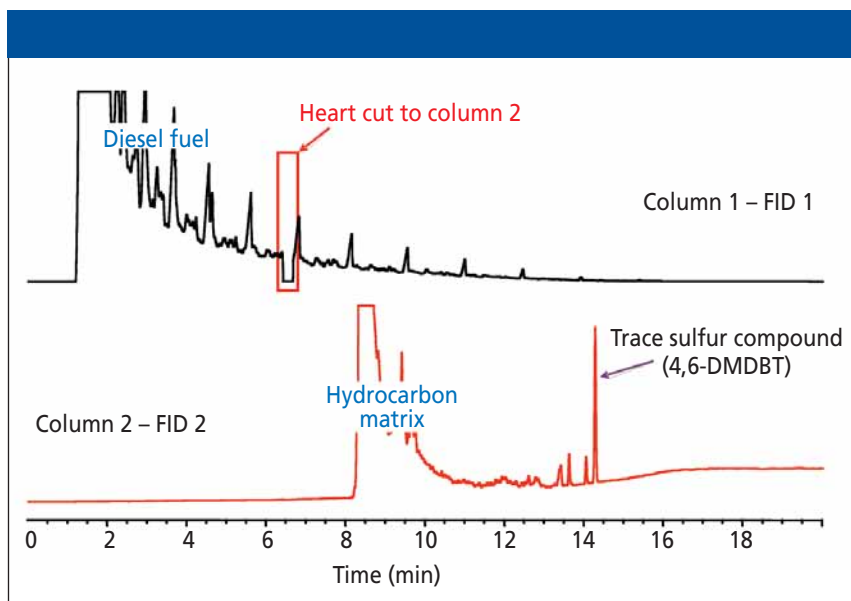


Figure 4: Separation of trace sulfur compounds in diesel fuel. In the initial chromatogram (HP-5 column), hydrocarbon peaks mask the 4,6-dimethyldibenzothiophene (4,6-DMDBT). By means of a Deans switch, the 4,6-DMDBT region is cut from the column 1 effluent and diverted to an Innowax column (Agilent Technologies) on which it is completely resolved from otherwise coeluted peaks.

Principal Capillary Flow Capabilities

GC applications afforded by capillary flow utilize one or more specialized connectors and manifold plates. Connectors can be functionally divided into two groups: those without and those with the capability to supply makeup gas. Typical types of passive connectors and examples of their application include butt connectors for connecting a precolumn ahead of the analytical column, tube connectors for connecting capillary columns to gas sampling valves, and unpurged tees without makeup gas that can be used to split the column effluent to two different GC detectors. Connectors with makeup gas supplied and controlled by the Aux EPC (described in the following) support diverse GC applications that require precise switching and partitioning of GC flows as well as a capability for backflushing. Figure 2 schematically illustrates some of the most useful of these flow-switching components.

Split flows to multiple detectors: The ability to add constant-pressure

makeup gas when splitting flows among multiple detectors is important, especially when one of the detectors is a mass spectrometer. Without makeup gas, there is a danger that the pressure at the split point can drop below atmospheric pressure, resulting in detector gases or the external atmosphere being drawn into the vacuum system of the mass spectrometer. To eliminate this possibility, Aux EPC is used to supply sufficient makeup gas to maintain the required pressure at the split. Figure 3 illustrates a typical application of a splitter with makeup gas.

Column quick swaps: Another advantage of using Aux EPC constant-pressure makeup gas is the ability to change the column in a GC–mass spectrometry (MS) system without requiring system cool down or venting of the MS vacuum system. During the column swap, purging by the flow of Aux EPC controlled makeup gas prevents external air from diffusing into the column opening. The connector employed for this purpose is joined directly to the mass spectrometer transfer line. Typically,

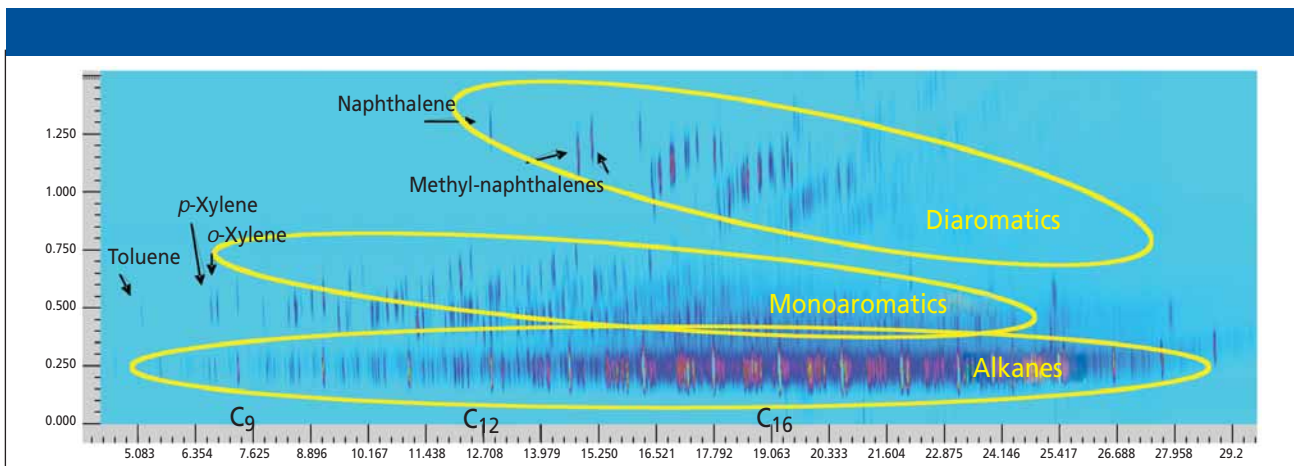


Figure 5: GC×GC analysis of diesel fuel. Special software developed for the purpose produces a 3-D plot. The first dimension displays hydrocarbon classes in clusters with their normal boiling point distributions, and the second dimension shows the separation of aromatics from the alkanes and the separation of the substituted aromatic groups.

this arrangement enables a column swap in about 3 min.

The Deans switch: This device is designed to actively switch the chromatographic flow to one of two ports, allowing the flow to be directed to an additional column and detector assembly or to be vented. Switching is done by changing the direction of the makeup gas with a solenoid valve located outside the oven. Unlike flow switching with rotary valves, the Deans switching mechanism is not wetted by sample flows or exposed to elevated temperatures. This minimizes component wear that causes eventual valve leakage and failure. Deans switch applications include heart cutting, a form of two-dimensional (2-D) GC in which a region of a chromatographic effluent is diverted to a second column (Figure 4). This type of configuration often is employed to identify peaks of interest in complex samples that can be masked by coeluted peaks or be present at trace levels. Heart cutting usually is limited to no more than five analyte peaks of interest because the elution of a diverted analyte must be completed before the next cut is taken. Deans switching also can be used to vent a part of a column effluent flow to protect detectors or columns from unwanted exposure to

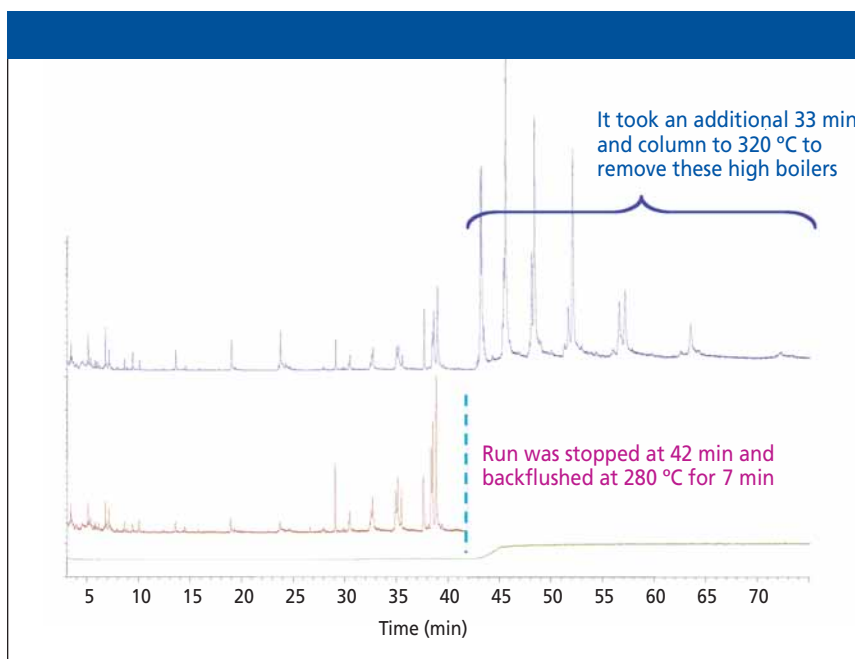


Figure 6: Backflushing reduces pesticide analysis cycle time for higher overall throughput. Top trace employing bakeout takes an additional 33 min at 320 °C to remove the high boilers that are eluted after the retention range of the analytes of interest. By using backflushing (bottom trace) all the high boiling components can be removed in 7 min at 280 °C.

specific solvents or reactive compounds. For example, the bead lifetime in a nitrogen–phosphorus detector can be extended greatly by venting chlorinated solvent peaks and excess derivatizing reagents before they reach the detector.

Modulator supported GC×GC: Capillary flow design can be used to make a pneumatic GC×GC modulator using an approach developed by Seeley and colleagues (7). The mod-

ulator is a specialized Deans switch equipped with a small storage volume that can be filled periodically with effluent from the first column and then switched, via a solenoid, thereby sweeping its contents at high flow rates into a second column. The process of alternately storing and then injecting portions of the first column effluent onto a second column is termed GC×GC. Results typically are displayed in a

3-D plot that simplifies visual identification of characteristic patterns of peaks and can highlight specific components-of-interest and their relative concentrations (Figure 5). The two-column system employed in GC×GC has a very large number of theoretical plates (calculated as the product of the plate number of the two individual columns) and yields a dramatic increase in resolution. Unlike thermal modulators, pneumatic modulation eliminates the need for cryogen.

Backflushing for increased sample throughput: Backflushing (Figure 6) is an efficient and time-saving alternative to column bake-out for removing high boiling sample components that are eluted after the peaks of interest. Any GC system equipped with a split-splitless or programmed temperature vaporizer inlet and either a QuickSwap, splitter (with EPC makeup), or Deans switch can be backflushed. After elution of the last

analyte, the inlet pressure is programmed to a low value and the makeup gas EPC is programmed to a high value. This reverses the flow through the column, which carries unwanted heavy sample components rapidly out to the split vent trap. Typically, column backflushing takes place in a fraction of the time required for bake-out and is done at a lower temperature. This increases sample throughput and reduces maintenance for both the column and detectors.

Conclusion

By combining several new techniques, in-oven devices for manipulating capillary column flows can now be constructed. These devices, when combined with enhanced EPC and calculation functions, provide many new capabilities and restore many desirable capabilities for capillary GC. These capabilities can now be implemented in routine GC labo-

ratories to solve a wide range of application problems.

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