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Review

Recent advances in flow-controlled multidimensional gas chromatography

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ABSTRACT

The continued development of flow-controlled two-dimensional gas chromatography (2-D GC) is reviewed, with a special emphasis on results published from 2001 through 2011. Heart-cutting 2-D GC continues to be used for isolating selected components in complex mixtures. The programmable and highly precise flows and temperatures produced by modern gas chromatographs have made it easier to selectively transfer analytes to the secondary column and to backflush unwanted components from the primary column. Several new Deans switch interfaces for performing heart-cutting 2-D GC have been introduced, with most attention given to devices that integrate the flow connections into a single unit. Heart-cutting 2-D GC has been used to isolate analytes in a wide variety of complex mixtures including fuels, industrial feedstocks, fragrances, and environmental extracts. Valve-based comprehensive 2-D GC (GC × GC) was also actively developed in the past decade. Valve-based modulation is a simple way to generate GC × GC separations without using cryogenic fluids. More than ten new valve-based modulators were introduced. Diaphragm valves fitted with sample loops are the most common low duty cycle modulators, whereas fluidic modulators that employ differential flow conditions are the most common high duty cycle modulators. Applications of valve-based GC × GC include analysis of hydrocarbon mixtures, essential oils, and environmental samples.

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1. Introduction

Single-column gas chromatography (GC) can produce high resolution separations, yet complex samples, like those associated with fuels, fragrances, and environmental extracts, often produce chromatograms with overlapping peaks. Adding a second GC separation is a common approach for increasing resolving power. The resulting analytical technique is classified as two-dimensional gas chromatography (2-D GC) when the secondary separation is performed while maintaining at least some of the original primary separation. The gases, flow controllers, sample inlets, columns, and detectors used for 2-D GC analyses are the same as those used for single-column GC separations. However, 2-D GC involves the use of a special device for controlling the transfer of compounds from the primary column to the secondary column. Experience has shown that the construction of this interface and the manner of its implementation are critical factors in the success of a 2-D GC analysis. There have been numerous reviews of 2-D GC published over the past decade [1–10]. This review focuses on recent advances with special attention given to 2-D GC separations conducted with valve-based interfaces as opposed to interfaces employing thermal gradients (e.g., cryogenic modulators).

2-D GC separations are categorized either as heart-cutting 2-D GC or as comprehensive two-dimensional gas chromatography (GC × GC). Heart-cutting 2-D GC separations pass a subset of the sample components to the secondary column and are best suited for the analysis of a few constituents. In contrast, GC × GC separations pass all sample components through both separation stages and are best suited for the complete analysis of composition.

2. Heart-cutting 2-D GC

2.1. Basic instrument setup

Heart-cutting 2-D GC is also referred to as multidimensional gas chromatography (MDGC) or conventional 2-D GC in the scientific literature. A schematic of a typical heart-cutting 2-D GC instrument is shown in Fig. 1. The sample mixture is first introduced at the head of the primary column. Carrier gas sweeps the sample components through the primary column toward the interface. The interface transfers the primary effluent to either a short capillary flow restrictor that leads to a detector or to the head of the secondary column. Components transferred to the secondary column, pass down its length until they reach a second detector. In heart-cutting 2-D GC, the primary column is also called the pre-column, and the secondary column is frequently referred to as the analytical column or the main column.

Heart-cutting 2-D GC is commonly employed in the following manner: standard mixtures containing only the compounds of interest (i.e., the analytes) are analyzed with the interface directing all of the primary effluent to the flow restrictor. Chromatograms obtained at the exit of the flow restrictor are then used to determine the primary retention times of the analytes. This information is used to program the interface to only direct primary effluent containing analytes to the head of the secondary column. An individual segment of primary column effluent introduced to the secondary column is called a heart-cut. Real samples are analyzed with the interface heart-cutting each analyte to the secondary column. The selectivity of the secondary column is chosen to separate analytes from sample matrix components that co-elute on the primary column. It is advantageous to make the individual heart cuts as narrow as possible to minimize the number of sample matrix components allowed to reach the secondary column. However, the heart-cuts must be wide enough to ensure that each analyte is quantitatively transferred to the secondary column.

2.2. The experimental requirements of a heart-cutting 2-D GC separation

Recent improvements to the instrumentation of single-column GC separations have made 2-D GC separations more feasible. The analyte must have a unique set of retention times on the primary and secondary column for a 2-D GC analysis to be successful. Thus, the solvation properties of the analyte must be significantly different from those of the interfering components and there must be a pair of stationary phases capable of exploiting this difference. Fortunately, a wide range of stationary phase selectivities are now available as many new stationary phases, such as ionic liquids and porous solids, have been recently introduced in capillary format. A successful heart-cutting 2-D GC analysis also relies upon highly reproducible retention times because primary retention time shifts will result in heart-cuts that do not quantitatively transfer analytes to the secondary column. Modern gas chromatographs are now equipped with electronic pneumatic controllers and heated zones that provide highly precise flows and temperatures. These advances have increased the precision of retention times.

There are some experimental requirements that are unique to 2-D GC. Heart-cutting 2-D GC relies upon the ability of the interface to transfer narrow segments of primary column effluent to the head of the secondary column. Ideally, this process can be performed without significantly broadening the primary column peaks. This goal can only be achieved if the interface has un-swept volumes that are less than the volume of a primary peak. A typical GC analysis produces peaks widths on the order of 0.1 min at flows of 1 mL min^{-1}. This means peaks have volumes of approximately 100 μL. Thus, the un-swept volume of the interface must be significantly less than 100 μL (e.g., <20 μL). Clearly bulky unions or large valves cannot be used. It is also important that the sample components do not stick to the internal surfaces of the interface device; thus, inert materials and surface deactivation are often required. It is often advantageous to perform multiple heart-cuts during a single chromatographic run. Primary retention time shifts will be generated if the act of heart-cutting disrupts the primary column flow. Such disturbances make it difficult to accurately predict the timing required for subsequent heart-cuts. Thus, switching the interface between the two

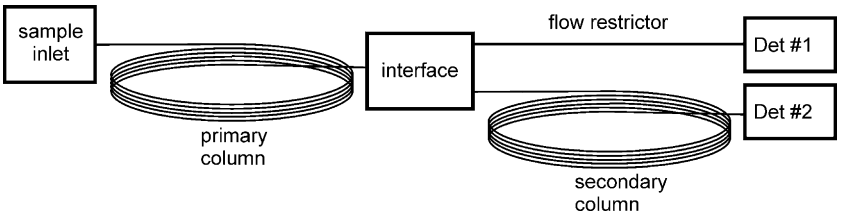

Fig. 1. Schematic of an apparatus for producing heart-cutting 2-D GC separations. Sample components are initially injected into the primary column. When sample matrix components emerge from the primary column they are directed by the interface to detector #1 through the capillary flow restrictor. When analytes emerge from the primary column, they are directed to the secondary column for further separation.