



High speed Deans switch for low duty cycle comprehensive two-dimensional gas chromatography



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ABSTRACT

A new high-speed valve-based modulator has been designed and tested for use in comprehensive two-dimensional gas chromatography (GC × GC). The modulator is a Deans switch constructed from two micro-volume fittings and a solenoid valve. Modulator performance was characterized over a wide range of device settings including the magnitude of the switching flow, the gap between the tips of the primary and secondary column, the primary column flow rate, and the carrier gas identity. Under optimized conditions, the modulator was found to be capable of generating narrow pulses (<50 ms) of primary effluent with a 2 mL/min secondary column flow. This capability will ultimately allow the modulator to be used with GC × GC separations employing a wide range of detectors and secondary column geometries. The main disadvantage of this modulator is that it employs a low sampling duty cycle, and thus it produces separations with sensitivities that are lower than those produced with thermal modulators or differential flow modulators. The efficacy of the new high-speed Deans switch modulator was demonstrated through the GC × GC separation of a hydrocarbon standard and gasoline. Precise quantitation of individual components was possible provided the modulation ratio was kept greater than 2.0.

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1. Introduction

Comprehensive two-dimensional gas chromatography (GC × GC) subjects the entire sample to a primary separation and a secondary separation. The modulator, a device situated between the primary and secondary columns, is critical for the production of GC × GC separations. The history and principles of GC × GC modulation technology have been described in two recent review articles [1,2]. The modulator samples primary column effluent and introduces it to the secondary column as a narrow pulse. This process is repeated throughout the analysis at an interval known as the modulation period. Component pulses can be generated by three different mechanisms: thermal modulation, differential flow modulation, and low duty cycle modulation.

Thermal modulation uses sharp temperature gradients to concentrate the primary column effluent. The trapped components are released as a pulse at the end of the modulation period by the application of a rapid temperature increase. The vast majority of published GC × GC studies have used thermal modulation [3]. Thermal modulation has two distinct advantages: it transfers all of the primary effluent to the secondary column in a very narrow pulse and it employs a low carrier flow rate (approximately

1 mL/min). The low carrier flow is compatible with a wide range of detectors and secondary column geometries. Thermal modulation increases both sensitivity and resolution, but it requires either a large amount of liquid cryogen and/or an elaborate cooling/heating apparatus.

Differential flow modulation operates by collecting, but not concentrating, primary effluent in a sample loop [4–6]. The collected components are rapidly flushed from the loop into the secondary column with carrier gas flowing at a high rate. Differential flow modulation is the second most frequently used modulation technique [3]. Differential flow modulation is capable of transferring all of the primary effluent to the secondary column. However, high carrier gas flows (>10 mL/min) are required. The elevated flow limits the use of microbore (≤0.18 mm id) secondary columns and also makes it difficult to directly couple the secondary column to a mass spectrometer (MS) unless multi-stage vacuum systems are employed [7,8]. The main advantages of differential flow modulation are that pulses can be produced with simple combinations of valves and fittings and that high sensitivity is generated when using detectors that can handle elevated carrier flows (e.g., the flame ionization detector). Several recent studies have split the flow at the exit of the secondary column sending a small portion of the flow to a mass spectrometer while the remainder is directed to a second detector [9,10]. This allows standard mass spectrometers to be used, however, the splitting limits sensitivity. There have also been studies [11] where the secondary column flow is split immediately

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after the modulator to produce greater chromatographic efficiency in the secondary column at the expense of sensitivity.

Low duty cycle modulation generates pulses by diverting small segments of primary effluent to the secondary column [5,12]. Primary effluent is only allowed to enter the secondary column for a brief interval at the beginning of each modulation period. The primary effluent is directed to an exhaust vent for the remainder of the modulation period. Low duty cycle modulation, like differential flow modulation, can be produced with a valve and a few fittings. However, unlike differential flow, low duty cycle modulation does not in principle require high secondary flows; thus, it is potentially compatible with a wider range of column geometries and detectors. Unfortunately, low duty cycle modulation only transfers a small fraction of the primary effluent to the secondary column. Thus, it produces lower signal intensities than separations employing thermal modulation or differential flow modulation. This limits the sensitivity of the analysis and can also reduce quantitative precision if the modulation period is larger than the widths of the peaks emerging from the primary column [13]. On the other hand, there are many separations that do not require the utmost sensitivity (e.g., the determination of the aromatic content of gasoline). Such separations can be effectively and reliably performed with a low duty cycle modulator.

This article focuses on developing an improved low duty cycle modulator. There have been two main devices used for low duty cycle modulation: the multiport valve and the Deans switch. Multiport diaphragm valves were used in the original demonstrations of low duty cycle modulation [12] and have been shown to be well suited for repetitive actuation at high speed. Unfortunately, diaphragm valves were designed to operate at temperatures less than 200 °C and, thus, they can constrain the upper temperature of the GC × GC separation unless special heating configurations are employed [14].

A Deans switch is a fluidic device that was originally developed for heart-cutting two-dimensional gas chromatography (2-D GC) [5,15–17]. A Deans switch is frequently constructed with a set of tee unions and a three-port solenoid valve. The tee unions are situated inside the GC oven between the primary and secondary columns. The solenoid valve is placed outside of the column oven and is used to control the point of introduction of an additional flow of carrier gas called the switching flow. The Deans switch operates in two states: the inject state where primary column effluent is directed to the head of the secondary column, and the bypass state where primary column effluent is not allowed to enter the secondary column. In 2007, Seeley et al. [18] used a Deans switch manufactured by Agilent Technologies, Inc. as a modulator for comprehensive two-dimensional gas chromatography. This Deans switch employed Capillary Flow Technology where the normal combination of discrete tee unions was replaced by a single, fully integrated assembly. The device was originally designed for heart-cutting 2-D GC and was not designed to be a GC × GC modulator. This is an important distinction as the switching speed needed for GC × GC modulation is substantially higher than that needed for conventional heart-cutting. Seeley et al. found that a fairly large switching flow of 9 mL/min was necessary to generate the narrow pulses required for GC × GC analysis. The switching flow was combined with the primary flow of 1 mL/min, and evenly split between a secondary column and the flow restrictor. This produced a secondary column flow of 5 mL/min; a value above the optimum for chromatographic efficiency. To compensate for the increased theoretical plate height, Seeley et al. employed a long secondary column (i.e., 2.5 m). Despite requiring an elevated flow, Deans switch modulation GC × GC was found to be an effective way to analyze the composition of gasoline [18] and to determine the levels of petroleum contamination in water and soil [19]. Separations were performed with temperatures as high as 320 °C. However, the high secondary flow imposes some

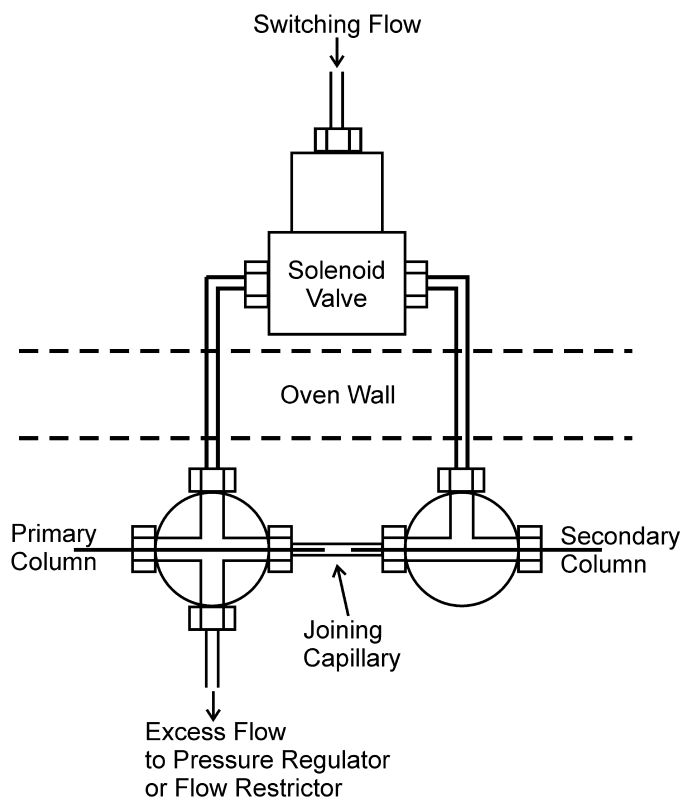


Fig. 1. Basic construction of the high speed Deans switch.

limitations. For example, the vacuum systems of most GC mass spectrometers cannot handle a 5 mL/min carrier gas load. In addition, a high secondary flow combined with a long secondary column make it difficult to employ a narrow bore (≤ 0.18 mm) secondary column due to the high head pressure that would be produced.

This article describes the development of a Deans switch designed specifically as a GC × GC modulator. The main goal is to make a Deans switch that can transition between the bypass and inject states on a timescale less than roughly 30 ms while employing a secondary column flow that maintains high chromatographic efficiency and is compatible with standard GC mass spectrometers.

2. Material and methods

2.1. Construction of the high speed deans switch

A schematic of the Deans switch is shown in Fig. 1. The device was constructed from a 1/32" cross union (VICI, ZX.5L) and a 1/32" tee union (VICI, ZT.5L). A 2.0 cm × 0.53 mm piece of deactivated metal capillary (Restek, MXT-Guard), referred to as the joining capillary, was held in place between the two fittings. The three port solenoid valve (Parker-General Valve, Part No. 009-0284-900) was connected to the fittings with two additional 0.53 mm id steel capillaries (Restek, MXT-Guard). An auxiliary flow of carrier gas, the switching flow, was introduced into the common port of the solenoid valve. The normally closed port of the solenoid valve was connected to the cross union and the normally opened port was connected to the tee union. The end of the primary column was fed through a graphite-velspel ferrule, into the cross union, and then into the joining capillary. The head of the secondary column was fed through a graphite-velspel ferrule, into the tee union, and then into the joining capillary. The distance between the tips of the primary column and secondary column was separated by a gap of approximately 2 mm, though this gap distance was varied in the initial

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