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New valve switching modulator for comprehensive two-dimensional gas chromatography

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Abstract

This paper describes a new design for a valve switching modulation system developed for comprehensive two-dimensional gas chromatography (GC × GC). This system is based on the differential flow and is different from the earlier reported in the literature. It has several advantages and constructed of inexpensive, commercially available parts that are easily installed on most gas chromatographs. Operation is easy and robust and requires no external coolants. This new design allows GC × GC analysis to be conducted in any laboratory environment capable of supporting conventional GC and imposes no additional consumable costs. The system is flexible and permits the use of a wide range of stationary phase combinations. The system has been successfully tested for complete material transfer and is suitable for quantitative analysis. The flexibility of this system is demonstrated using several test mixtures that show its extended application in petroleum, biochemistry, and environmental studies.

Keywords: Comprehensive two-dimensional gas chromatography; Differential flow modulation; Valve switching modulation; Modulation design

1. Introduction

Comprehensive two-dimensional gas chromatography (GC × GC) is a new development in separation technology [1,2]. This technique provides higher resolution, better sensitivity, and larger peak capacity. In order to achieve this two-dimensional separation, a modulation unit is required to gate the material that continuously comes out from the end of the first column and transfer this gated material to the front of the secondary column. Many reported systems [1–9] use a form of thermal modulation where continuous flowing coolant gas traps the materials eluting from the first column and pulsed hot gas flow regulates the release. Liquid carbon dioxide or liquid nitrogen is used as coolants. Although both are not toxic, they are pressurized hazardous materials that require care when shipping and handling and may not be readily available in remote locations or suitable for use in a manufacturing environment.

Differential flow modulation [10,11,13–15] is an alternative design that is based on switching valves and the regulating the secondary column flow to achieve the gating function needed in comprehensive two-dimensional gas chromatography. Several different designs of differential flow modulation [11–15] achieve complete transfer of material from the first column to the second column. Differential flow modulations eliminate the need for coolants, lower consumable expense, and are generally easy to operate and maintain. However, several of designs published in the literature [10–15] have several disadvantages that limit their use. Examples of this include relative long-modulation time that degrades the resolution in the first dimension [13] and having little flexibility in the experimental conditions [7].

In this study, a new differential flow modulation unit was designed [16] using two four-ports, two-position, switching valves. The goals of this design were to construct a modulator from easily installed, readily available components that offers the performance and flexibility of thermal modulators. This modulation system is extremely attractive because of its simplicity. It uses no coolant gases, and provides a means of conducting GC × GC in any laboratory environment currently capable of simple GC analysis.

The performance of this new differential flow modulation design is demonstrated on four different types of samples: two hydrocarbon mixtures with different boiling point temperature range, a mixture of fatty acid methyl esters (FAMEs), and

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a polychlorine-substituted biphenyl (polychlorinated biphenyl, PCB) mixture. The efficiency of this new design for complete material transfer from the first column to the second column is tested to determine if the modulator is suitable for quantitative analysis.

2. Experimental

2.1. Sample preparation

2.1.1. n-Alkane test mixture

Two sets of *n*-alkane mixtures, one with carbon number distribution between C_7 and C_{15} and the other one with carbon number distribution between C_{10} and C_{24} were prepared by mixing equal weights of each *n*-alkane compound in carbon disulfide. The pure *n*-alkanes were purchased from Aldrich (Milwaukee, WI, USA).

2.1.2. Petroleum refinery streams

Two petroleum streams collected from the catalytic cracking of heavy oil were used in this study. One, with carbon number distribution from C_5 to C_{14}, is a naphtha stream collect in the gasoline temperature range (∼40 °C to ∼260 °C). The other, with carbon number distribution from C_8 to C_{25}, is a diesel stream collected between 170 °C and 410 °C. These refinery samples were used without any further treatment.

2.1.3. Lipid standards

A lipid standard was purchased from Aldrich (part number: 18919-1AMP). It is a mixture of FAMEs with alkyl carbon chain length distribution from C_4 to C_{24}. The sample was diluted with 0.5 mL carbon disulfide solvent for GC × GC analysis.

2.1.4. Polychlorine-substituted biphenyl (PCB) mixture

A PCB reference standard mixture for US Environmental Protection Agency (EPA) methods 525 and 525.1 was purchased from Aldrich (part number: 48246). It is a mixture of chlorine-substituted biphenyl with the number of chlorine atoms varying from one to eight. The original solvent was replaced with carbon disulfide for GC × GC analysis.

2.2. Instrumentation

2.2.1. Modulation design

The modulation system was assembled using two four-port, two-position, switching valves in combination as illustrated in Fig. 1. The valves, rated for maximum operation conditions of 350 °C and 300 psi, are equipped with an electrical actuator (VICI Valco Instruments, Houston, TX, USA, part number: EH6C4WT). Both switching valves were installed on an Agilent 6890 gas chromatograph (Agilent Technologies, Wilmington, DE, USA) configured with a 100-tray autosampler, flow modulators, a split/splitness inlet, and a flame ionization detection (FID) system. The transfer lines are a set of pre-cut 1/16 in. stainless steel tubing with 1.0 mm I.D. and 30 cm length (actual length is 29.5 cm, part number: W-141, Upchurch Scientific,

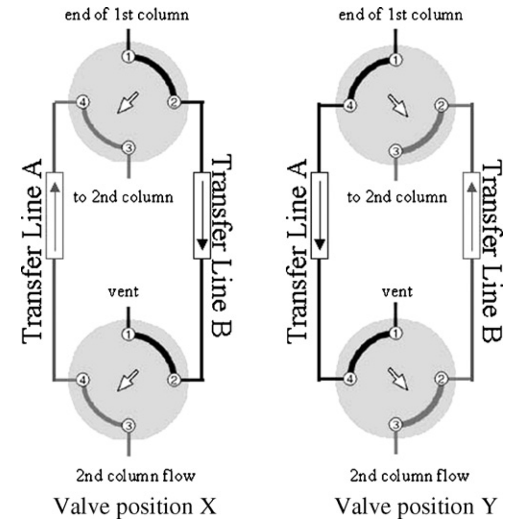

Fig. 1. The modulation system design with combination of two four-port, two-position valves.

Oak Harbor, WA, USA). Other materials can be used as transfer line such as deactivated capillary columns. However, all the material used in the modulator may interact with certain types of analytes, for example, the stainless steel valve body may interact with acid type of analytes. A programmable digital valve sequence box (VICI Valco Instruments, part number: DVSP4) is used to control the modulation interval. A start–stop key in the valve sequence program box is modified and connected to the gas chromatography remote start–stop socket to synchronize the valve switching with the injection.

Fig. 2 is a photograph of this modulation assembly in the GC system. The valves are installed inside the GC oven with the electrical actuator sticking out from the top. The programmable digital valve sequence box is located on top of the GC system. There is no specific requirement where the valves are mounted, as long as the modulation function can be properly performed. Mounting the valves and actuators on the side may be necessarily to accommodate the design of other gas chromatographs.

The modulation system is set up between the first and the second dimensional columns. The first dimensional column used is a weak-polar column (BPX-5, 30 meter, 0.25 mm I.D., 1.0 μm film), and a polar column (Sol-Gel Wax, 3 m, 0.53 mm I.D., 1.0 μm film), used as the second column. Both columns were purchased from SGE (Austin, TX, USA). The two separation capillary columns are supported inside the oven in the same manner as the traditional GC system.

2.2.2. Data acquisition and processing

Agilent Technologies Chemstation is used for instrument control and data acquisition. The modulation period was 8 s. The sampling rate for the detector was 100 Hz. After data acquisition, data were further processed for qualitative and quantitative analysis. The qualitative analysis is to convert data to a two-dimensional image that is processed by a program called "Transform" (Research Systems, Boulder, CO, USA). The two-dimensional image is further treated by "PhotoShop" program (Adobe System, San Jose, CA, USA) to generate publication-