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Development of a new consumable-free thermal modulator for comprehensive two-dimensional gas chromatography

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ABSTRACT

A simple and cost-effective GC × GC modulator requiring no moving parts or consumables, hence suitable for field analysis and monitoring, was developed. The modulator was constructed from a specially designed Silcosteel® trapping capillary, installed outside the GC oven, and coated inside with polydimethylsiloxane (PDMS) stationary phase. Dual-stage modulation was accomplished by resistively heating alternate segments of the trap with a custom-designed capacitive discharge power supply. The performance of the proposed modulator was comparable to many GC × GC systems currently in use, with the injection band widths as low as 60 ms at half height. With proper selection of the stationary phase in the trap, the modulator can be used for the analysis of complex mixtures with volatility range spanning from *n*-C5 to *n*-C40.

1. Introduction

Comprehensive two-dimensional gas chromatography (GC × GC) significantly increases peak capacity and resolution, improves mass sensitivity and generates structured three-dimensional chromatograms. This is accomplished by subjecting the sample to separation in two columns, or dimensions, coated with stationary phases differing in their selectivity. The two columns are coupled through a special interface, or modulator, which ensures that all sample components are subject to separation in both dimensions, and that separation accomplished in the first dimension is preserved in the second dimension. Regardless of the interface type or design, the modulator traps or samples compounds eluting from the first dimension column and periodically injects them as narrow pulses into the second dimension column for further chromatographic analysis. GC × GC has been successfully used in applications ranging from petrochemical analysis and forensics to environmental, health and food analysis. Readers interested in GC × GC instrumentation are directed to review papers, e.g. [1–3].

All existing GC × GC interfaces can be broadly categorized as thermal or valve-based. Heater-based and cryogenically operated modulators are considered subclasses of thermal interfaces. While valve-based interfaces are gaining in popularity and can be a good choice for portable and cost-effective GC × GC instrumentation, description of their operation is beyond the scope of this paper, and details can be found in the literature, e.g. [4–7].

The first GC × GC modulator was reported in 1991 by Liu and Phillips. It was of the heater-based type [8]. This simple interface consisted of a segment of a thick-film fused silica capillary, with the outer surface coated with gold paint. Modulation of analytes was accomplished by periodical resistive heating of the gold-painted trap. While this interface provided a proof-of-concept, it was far from ideal, as the injection bands onto the second column were broad and irregular. Later, Phillips and co-workers developed and commercialized the rotating thermal modulator [9,10]. Similarly to his original model, trapping and focusing of analytes exiting the first dimension was accomplished with a thick-film capillary; however, instead of using direct resistive heating to remobilize and inject the analytes into the second dimension column, a rotating thermal heater was implemented. While this modulator produced better results and was generally more robust, it suffered from drawbacks associated with the moving parts. Later, an interface consisting of resistively heated Silcosteel® trapping capillaries packed with a microsorbent bed was developed in our laboratory [11]. Burger et al. also developed a thermal heater-based interface that consisted of a thick-film capillary column encased by a steel jacket, allowing for multi-stage trapping that mimicked the rotating thermal modulator [12]. However, the inability of heater-based modulators to effectively trap volatile compounds and to quickly release

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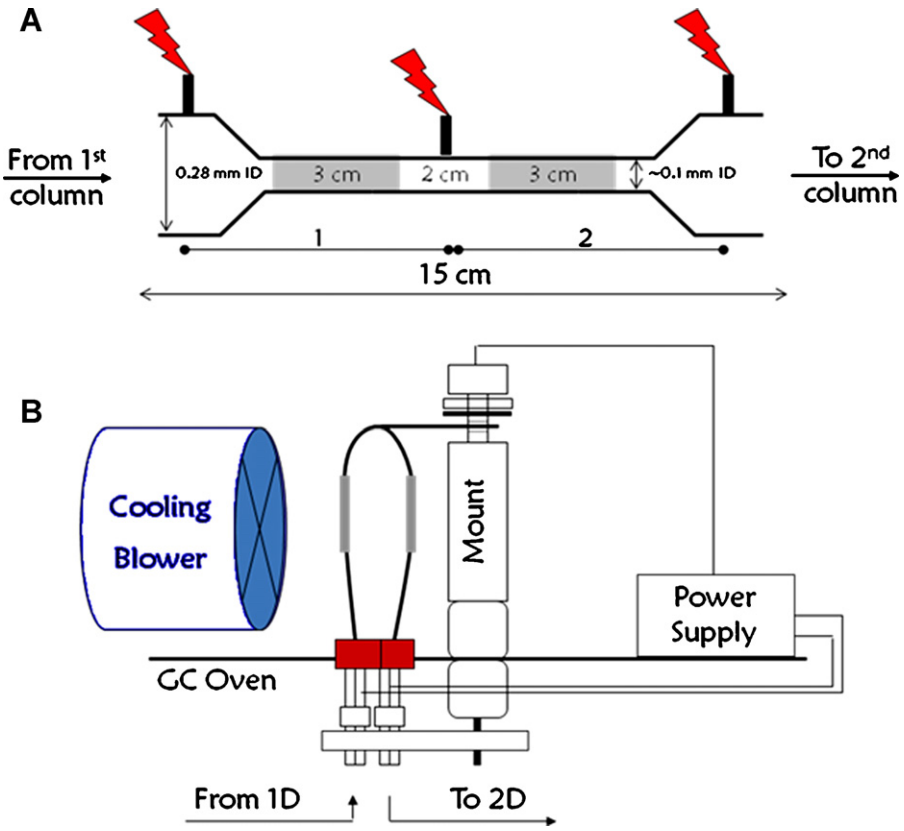

Fig. 1. Schematic diagrams of the modulator: (A) The flattened trapping capillary with two trapping zones (areas with intact stationary phase, shown in gray). Electrical contacts at 3 points ensure dual-stage modulation via alternative resistive heating. (B) The trap installed atop the GC oven and secured in place with two GC septa. The cooling blower was in close vicinity of the trapping capillary (~1–3 cm) and was continuously operated during the analysis. Two electrical contacts were located at the stainless steel unions inside the oven, while the middle contact was supported by the middle mount.

semi-volatile compounds at the allowed desorption temperatures led to their discontinued use. Presently, all commercially available GC × GC systems are either cryogenic or valve-based.

Around the time that Phillips reported the development of the rotating thermal modulator ("sweeper"), Kinghorn and Marriot constructed the first cryogenic modulator, the longitudinally modulated cryogenic system (LMCS) [13]. In cryogenically operated GC × GC instrumentation, analyte trapping is achieved by cooling a short segment of a column with a cryogenic agent (liquid CO_2 or N_2, or gas cooled with LN_2), and remobilization of the band is accomplished by rapidly heating the trap with a hot jet or by removing the source of cold temperature to allow the trap to quickly reach the oven temperature.

Even though the LMCS proved to be reliable over time, the use of moving parts was considered a drawback. Complementary research efforts were aimed at interfaces with no moving parts and colder cryogenic consumables. For example, interfaces utilizing LCO_2 [14] and liquid nitrogen (LN_2) [11] with no moving parts enabled the analysis of the most volatile analytes. Following this, various cryogenic interfaces were developed and commercialized [15–17].

Although cryogenic modulators are considered the most effective and have in fact contributed to the majority of applications to date, the commercial GC × GC systems are not universal in nature; indeed, every modulator has distinct advantages and limitations. Cryogenically operated GC × GC interfaces require a constant supply of LCO_2 or LN_2, which make them costly to operate and impractical for field analysis. It is likely therefore that the transition of GC × GC instrumentation from the research sector to routine laboratories or into the field will depend on the development of systems that are simple, robust, cost-effective, devoid of cryogenic consumables, and field transportable. Satisfying such criteria requires further research efforts focused on the development and engineering of interface technology. A consumable-free cryogenic system was introduced relatively recently by LECO based on the work of Libardoni et al. [18], but it is not suitable for the analysis of the most volatile fractions. Agilent introduced a differential flow modulator based on the work of Seeley et al. [19], but it works effectively only for short modulation periods, hence offers limited separation space in the second dimension. In addition, it cannot be easily coupled to a mass spectrometer because of the high carrier gas flow required in the second dimension (~20 mL/min). The goal of this research was to develop a cryogen-free modulator with no moving parts which could be used for a thermal desorption comprehensive two-dimensional gas chromatography system for in situ measurements of the semi-volatile fraction of organic aerosols (so-called 2D-TAG) [20]. While that contribution introduced only the basic principle of operation of the modulator, this paper focuses on its detailed characterization.

2. Experimental

The design of the modulator is depicted in Fig. 1. The interface consists of a flattened Silcosteel® trapping capillary, a cooling blower, and a custom-designed capacitive discharge power supply. Dual-stage modulation is carried out in the following manner: analytes eluting from the 1D column enter the trapping capillary, whose lower temperature promotes their partitioning into the nonpolar stationary phase. This accomplishes analyte trapping and