Sensors and Actuators B 231 (2016) 135–146

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

First-principle modeling and characterization of thermal modulation in comprehensive two-dimensional gas chromatography using a microfabricated device

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ARTICLE INFO

Article history:
Received 5 March 2015
Received in revised form 10 February 2016
Accepted 26 February 2016
Available online 3 March 2016

Keywords:
GC × GC
Comprehensive two dimensional gas chromatography
Thermal modulator
MEMS
Simulation and validation
Modeling
COMSOL simulation

ABSTRACT

Thermal modulation of analyte effluents at a junction between serially connected complementary columns is a critical process in comprehensive two-dimensional gas chromatography (GC × GC). However, little effort has been made to theoretically study this process with a full understanding of key phenomena. We developed a theoretical model of single-stage thermal modulation processes based on fundamental physics of gas chromatography (GC) with the aim to elucidate factors leading to improvements in GC × GC analyses. Model predictions were compared with experimental data obtained using our microfabricated thermal modulator (μTM) operating as a single-stage thermal modulator. Built upon one-dimensional (^{1}D) GC theory, our model predicted the temporal and spatial distribution of analyte concentration within a thermal modulator (TM) channel during periodically repeating modulation cycles, each consisting of a cooling and heating period and yielding sharp peaks from a broad first dimension peak. Our model incorporated the effect of the location of the incoming ^{1}D Gaussian peak to the μTM, with respect to the onset of the cooling period and the influence of cold interconnects on the thermal modulation process. Excellent match between experiment and simulation was obtained. Finally we proposed a few design modifications which could drastically improve performance of our μTM.

1. Introduction

Resolving analytes in highly complex mixtures poses a significant challenge for analytical chemists. Peaks of such complex mixtures tend to overlap each other, a phenomenon known as co-elution. Securing large peak capacity commonly entails increasing the column length, decreasing the column diameter, or a combination of both [1–7]. The use of a column with such a great excess of peak capacity can ease some of the problems but the costs are high in terms of analysis time, detection limits and instrument requirements. In contrast, two-dimensional gas chromatography (GC × GC) is a promising alternative approach that enables complex mixtures to be resolved with higher separation capacity and selectivity than the conventional approach described above. Furthermore, the GC × GC technique potentially permits development of a miniaturized GC lab-on-a-chip system incorporating a microfabricated thermal modulator (μTM) for real-time field deployment under limited resources without the separation performance compromised by reduced column lengths [8–12].

In GC × GC, two columns with different separation mechanisms, namely the first dimension (^{1}D) column and the second (^{2}D) dimension column, are used to separate the gas species (Fig. 1). The additional dimension enhances the peak capacity of the system, as a result of which a much higher number of compounds can be separated and analyzed. Various different column combinations have been tried since the 1990s [13], such as a combination of non-polar coating in the ^{1}D column and a polar coating in the ^{2}D column [14,15]; a polar coating in the ^{1}D column and non-polar coating in the ^{2}D column, [16–19] and various degrees of polarity in the ^{1}D column and ^{2}D column [20]. A combination of a non-polar ^{1}D column and a polar ^{2}D column is one of the most popular combinations used. The use of a non-polar column permits virtually direct transfer of methods that have already been developed in the context of conventional GC. Analytes in the same homologous group are separated in the ^{1}D on the basis of their different volatilities. In the ^{2}D, separation happens due to both boiling point and polarity. How-

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http://dx.doi.org/10.1016/j.snb.2016.02.132
0925-4005/

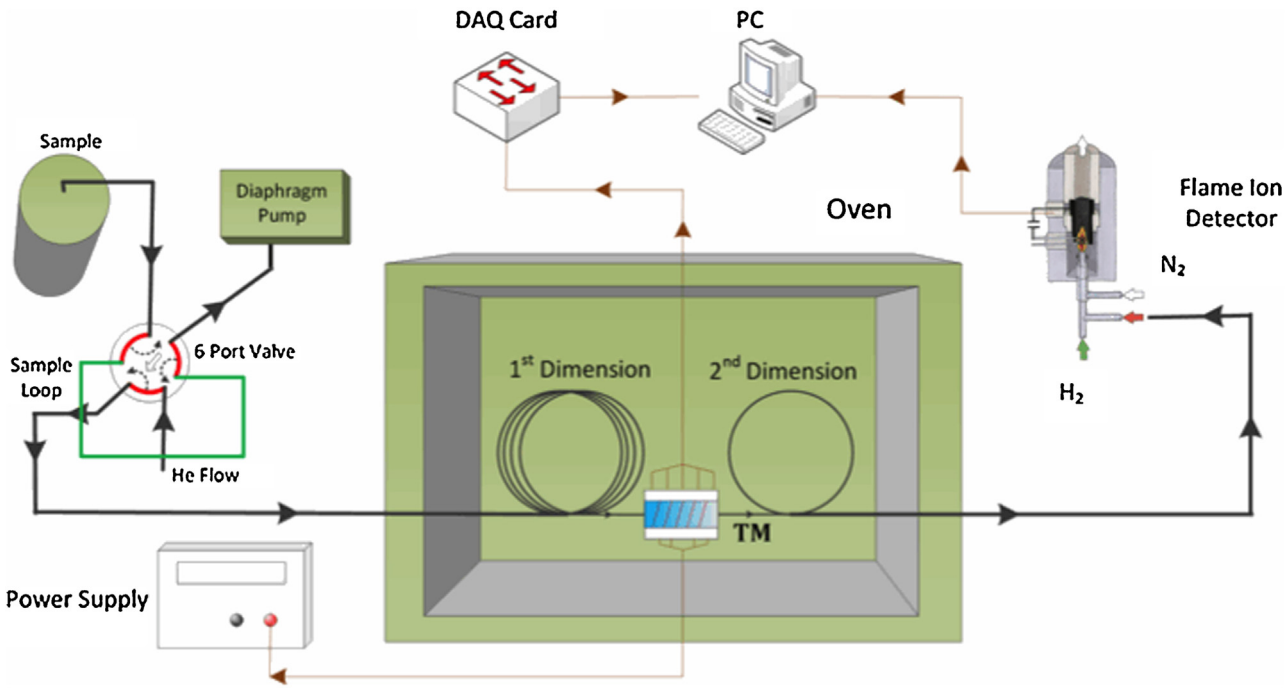

Fig. 1. Schematic of a typical GC × GC system incorporating thermal modulator (TM) and two columns with their internal surfaces coated with complementary stationary phases for analyte separation. Additional components of the system include a sample injection unit, a temperature-controlled oven, a gas sensor (flame ionization detector), a computer system for programmable TM operation and data acquisition, and a power supply.

ever, any boiling point contribution to the ^{2}D retention time can be neutralized by temperature ramping on the ^{2}D; as a result, separation is primarily governed by specific polarity-based interactions [14]. That is, the two chromatographic processes are complementary to each other, and the separation is orthogonal. More recently, it has been found that a polar/medium polar ^{1}D and a polar ^{2}D column can provide valuable results especially when highly polar and semi-polar analytes such, as alcohols, aldehydes, ketones, esters and acids, are among the key components of the mixture [20,21].

An intermediate modulator device placed at the junction between the ^{1}D and ^{2}D plays a key role in realizing GC × GC analyses (Fig. 2A) [22,23]. While different types of modulators exist, thermal modulators (TMs) have become widely used due to their ability to provide comprehensive modulation resulting in increased analyte detectability relative to other modulator types [24–30]. The injected mixture is partially separated in the ^{1}D, and arrives at the interface between the ^{1}D and the μTM (Fig. 2B). This device cuts and re-concentrates the effluent peak from a long ^{1}D column, at a time interval known as the modulation period (P_M) and re-injects them onto a short ^{2}D column as sharp sub-bands [31]. This prevents recombination of the species that have been partially separated in the ^{1}D after their re-injection to the ^{2}D. Further, focusing the sections of the ^{1}D effluent and re-injecting them into the ^{2}D greatly increases the peak height, whereby enhancing the detection limit relative to the noise threshold of the detector (Fig. 2C). Mapping the obtained signal peaks with respect to both the ^{1}D retention time and the ^{2}D retention time results in the two-dimensional (2D) gas chromatogram and allows for high-resolution analysis of complex gas compound mixtures at large capacity (Fig. 2D). Based on this transformation, a ^{2}D contour plot is obtained and is subsequently used to identify any compounds present in the original mixture (Fig. 2E). However, Blumberg, Blumberg et al. [32,33] show that while the theoretical peak capacity of GC × GC is much higher than that of the conventional GC, current experimental studies show GC × GC only achieves moderately improved separation capability. Only under highly optimized conditions leading to modulated peaks at a FWHH of <20 ms, can the theoretical maximum peak capacity be obtained. Further, if the FWHH of the modulated peaks approaches 100 ms, the effective gain becomes 1. While GC × GC still yields a few secondary benefits with broader modulated peaks, such as group-type identification/structured chromatograms [34], higher sensitivity, and large peak amplitudes [35], the primary benefit of GC × GC over conventional GC in terms of peak capacity becomes less obvious [36]. Hence, the modulator device is the key bottleneck in reaching the desired separation performance of GC × GC. To reach the maximum possible potential of GC × GC operated by thermal modulation, a TM needs to inject very sharp effluent bands with full-width at half height (FWHH) as narrow as 10 ms into the ^{2}D with a short channel length of 1–2 cm at a flame ionization detector (FID) data acquisition rate of ~ 1 kHz [32,33,36]. Hence, there is significant room for improving the peak capacity obtainable using GC × GC by optimizing the performance of the modulator to realize the ideal GC × GC operation above. Since, the FWHH of the modulated peak is the critical parameter determining the effective peak capacity of the GC × GC system, we use that as the performance metric of the system in our study.

To our best knowledge, no rigorous theoretical model exists that provides a good design guideline for TMs. This prevents researchers from achieving optimal performances for TMs based on a thorough understanding of physics governing the thermal modulation process. Hence, they usually resort to the expensive route of reducing the minimum trapping temperature, with the aim to achieve small FWHH of injection. This paper presents a theoretical basis to predict the behavior of a microfabricated TM device (μTM) developed in our previous study [8,9]. The goal of this paper is to understand the physics governing the operation of the device, so as to develop better and more efficient μTMs in the future. While our original μTM is a two-stage device as described later in Section 2.2, we have operated it as a single-stage device, where the both stages are synchronously operated with no time lag between the heat pulses applied to the stages, and developed a model for the microscale thermal modulation process based on the first principles