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Review article

Comprehensive two-dimensional gas chromatography: A perspective on processes of modulation

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ABSTRACT

The first comprehensive two-dimensional gas chromatography (GC × GC) experiment was reported about 25 years ago [J. Chromatogr. Sci. 29 (1991) 227–231]; the GC × GC process was made possible by the development of a transfer device, defined as modulator. The process of modulation enables the isolation of effluent segments from the first column, and their re-injection onto the second column, in a continuous and sequential manner throughout the analysis. Over the years, many types of modulation systems have been introduced, each with specific advantages and disadvantages. Cryogenic systems are, at present, the most popular devices and represent the most effective form of modulation.

The present contribution is focused on possible future scenarios, with respect to modulation, and as a consequence related to comprehensive GC, in general. The development of new forms of modulation may open the road to a more widespread use of GC × GC technologies.

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1. Introduction

Gas chromatography (GC) was first described by James and Martin in 1952 [1]. A 100-min separation of 8 fatty acids on an 11-ft packed column (T = 137 °C) was shown. One could conclude, after a visual evaluation of the result of such outstanding work, that between 20 and 30 peaks could have been potentially-fitted in the one-dimensional (1D) separation space (peak capacity) generated by the instrumentation used, and the experimental conditions applied. Shortly after the invention of GC, the concept of open-tubular capillary (OTC) columns was introduced by Golay [2]. The low flow resistance offered by open capillaries enabled the use of longer GC columns, and the generation of more space for separation. Capillary columns were initially made by using stainless steel, and at a later stage by glass [3]. The high fragility of glass columns hindered the wide diffusion of these high-resolution separation tools; when fused silica was exploited as a material to fabricate columns in 1979 [4], the expansion of capillary GC underwent a great increase, due to the high flexibility and robustness of fused silica, among other characteristics. In general, a 30 m × 0.25 mm ID column can be expected to generate a peak capacity usually in the range of 400–600.

Comprehensive two-dimensional GC (GC × GC) was first reported in 1991 [5]; the technique is now well-known [6], has been used in various research fields [7–10], and will not be herein described. There is quite a lot of debate and divergent opinions on GC × GC peak capacity, and again, no discussion will be made on such a topic. However, and again in general, it can be affirmed that GC × GC methods can potentially generate an increase in peak capacity of at least one order of magnitude compared to 1D OTC GC approaches [11]. One could conclude that many samples amenable

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to GC analysis were elucidated the first time with packed-column GC, and then re-investigated once by using an OTC column, and a second time through GC × GC.

The object of the present contribution is not to exalt the superior peak capacity of comprehensive 2D GC, but to discuss about processes of modulation. It is the present author's opinion that some of the reasons behind the lack of widespread diffusion of the technology within the GC community can be related to the processes of modulation. As aforementioned, fragility was the main technological drawback of glass capillary columns. Now, the question is where does the "fragility" of GC × GC lie? Even though GC × GC is certainly not a novel technology, it is still perceived as such, mainly due to its limited use. Probably there are several reasons for such a situation, such as: I) high initial instrumental + software cost; II) greatly increased complexity related to method optimization and to the use of GC × GC software; III) enhanced operational costs (especially if cryogenic fluids are used); IV) the revolutionary nature of the overall technique (*e.g.*, chromatograms are visualized in a 2D/3D format, data processing); V) even the complex appearance of the instrumentation (*e.g.*, the presence of bulky Dewars, consumable-free cooling units, additional external tubing, modulation control systems, *etc.*). Reason IV is an intrinsic feature of the methodology, while the remaining characteristics are related, at different levels, to the modulation process.

2. The modulation approaches

Modulation approaches can be classified into three groups, based on manipulations of phase-ratio, temperature and flow. Brief historical aspects related to each group follow. For more thorough details on modulator evolution the reader is directed to the literature [12].

2.1. Phase-ratio modulators (PRMs)

The first types of modulator were based on phase-ratio focusing, and thermal desorption; in the first GC × GC work [5], the dual-stage modulator was constructed by coating the initial part (15 cm) of the second column (1 m × 0.1 mm ID × 0.5 μm d_f) with gold paint and by looping it outside the GC oven. The analytes eluting from the first column (21 m × 0.25 mm ID × 0.25 μm d_f) encountered a thick film of stationary phase at ambient temperature, and hence were entrapped. Re-mobilization of the focused chromatography band was performed through thermal desorption, a process induced by electrically-heating the gold coating. A scheme of a GC × GC instrument [with flame ionization detection (FID)], reported by Liu et al., is illustrated in Fig. 1 [13].

The thermal sweeper was the first commercial device, and is now obsolete. It was a moving modulator, inasmuch that it consisted of a slotted heater that rotated periodically over a section of capillary containing a thick stationary-phase film [14]. The accumulation process was performed inside the GC oven exploiting the low phase ratio of the column segment; re-injection was carried out through thermal desorption, a process which occurred when the heater passed over the same column segment.

2.2. Cryogenic modulators (CMs)

Cryogenic modulation was first introduced in 1998 by Kinghorn and Marriott, who reported the use of the longitudinally-modulated cryogenic system (LMCS) [15]. In previous research, the LMCS was described as a device capable of enhancing sensitivity [16]: the detector-end part of a capillary was passed through a cryo-trap, fed with a flow of CO_2 to generate intense cooling. At the end of the entrapment process, the longitudinal movement of trap

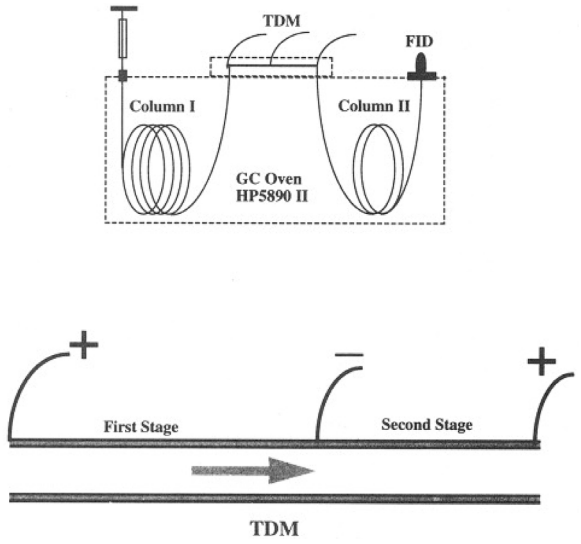

Fig. 1. Scheme of a GC × GC-FID system proposed by Liu et al. [13], along with an expansion of the modulator.

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exposed the re-concentrated analyte band to the GC-oven temperature, enabling solute re-injection onto the final part of the column. GC × GC analysis was achieved when the LMCS was operated at the head of a second analytical column [15].

In 2000, Ledford proposed a static dual-stage modulator, with two cooling (liquid N_2) and two heating (air) jets [17]. The jets were operated in an alternate manner, and were positioned at the head of the second column. One pair of heating/cooling jets was located at an upstream point of the second column, while the other pair was positioned at a downstream point. Soon after the introduction of the quad-jet device, Ledford et al. described a further dual-stage liquid N_2 system, characterized by a cold and hot jet [18]. Upstream and downstream cooling/heating spots were creating by looping a segment (1–1.5 m) of intermediate column (delay loop). The quad-jet and loop-type modulators are the most commonly-used CM systems.

2.3. Flow modulators (FMs)

Flow modulators belong to one of two categories: I) "in-line" valve systems, characterized by the presence of a switching valve with a direct connection with the first and second analytical column; II) "out-of-line" valve systems, specifically those which derive from the Deans switch principle and are thus based on manipulation of the pressure between the two GC dimensions [19]. The first FM GC × GC experiment was reported in 1998 [20], and was an in-line valve one (4 ports of a 6-port diaphragm valve were used). A modulation period of 500 ms was applied: the primary-column effluent was directed to the second column for 50 ms, while for the remaining 450 ms a separation was carried out on the second column and the primary-column effluent was directed to waste. Apart from the reduced sensitivity, a further disadvantage was the low maximum operational temperature of the valve. In 2006, the same research group introduced a 100% transfer in-line valve modulator [21]: a high-speed, 6-port, diaphragm valve, equipped with an accumulation loop, was mounted face downwards on top of a GC oven; only the ports (one port was plugged) were located in the oven. During the accumulation period, the primary-column effluent was compressed in the loop, with such an effect occurring because the downstream side of the loop was in connection with