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Review

Qualitative and quantitative approaches in comprehensive two-dimensional gas chromatography

Jacolin A. Murray*

Analytical Chemistry Division, National Institute of Standards and Technology, 100 Bureau Dr., Mail Stop 8392, Gaithersburg, MD 20899-8392, USA

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ABSTRACT

Comprehensive two-dimensional gas chromatography (GC × GC) offers advantages over one-dimensional gas chromatography (GC) including, high peak capacity, signal enhancement, and structured chromatograms. These advantages have been exploited to solve several analytical problems that are difficult to achieve in GC. In this review, qualitative and quantitative approaches of GC × GC are explored, including targeted, non-targeted, group, and fingerprinting analysis.

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Contents

1. Introduction

Comprehensive two-dimensional (2D) gas chromatography (GC × GC) is a technique that allows for the separation of an entire sample by two independent GC columns. This technique was first successfully achieved by Liu and Phillips in 1991 by incorporating a thermal modulator between the two columns [1]. The function of the modulator is to trap, focus, and inject small fractions from the first column into the second column. Implementation of the modulator allowed for retention of the separation in the first-dimension, achieving true comprehensive chromatography. Fig. 1 shows a block diagram of the components of GC × GC. The detector in GC × GC records a series of 2D chromatograms that can be transformed into a three-dimensional (3D) chromatogram as illustrated in Fig. 1. There are many reviews in the literature describing the fundamentals of GC × GC [2–11].

According to the literature, the three main advantages of GC × GC over one-dimensional (1D) GC are (1) potential for higher peak capacity, (2) signal enhancement due to analyte refocusing in the modulator, and (3) the ability to produce "structured" chromatograms [12–14]. Due to these advantages, GC × GC has been used in different applications to solve different problems that are not easily accomplished through 1D GC. The scope of this review is to examine the concepts and principles of GC × GC that are

* Tel.: +1 301 975 4116; fax: +1 301 977 0685.
E-mail address: jacolin.murray@nist.gov

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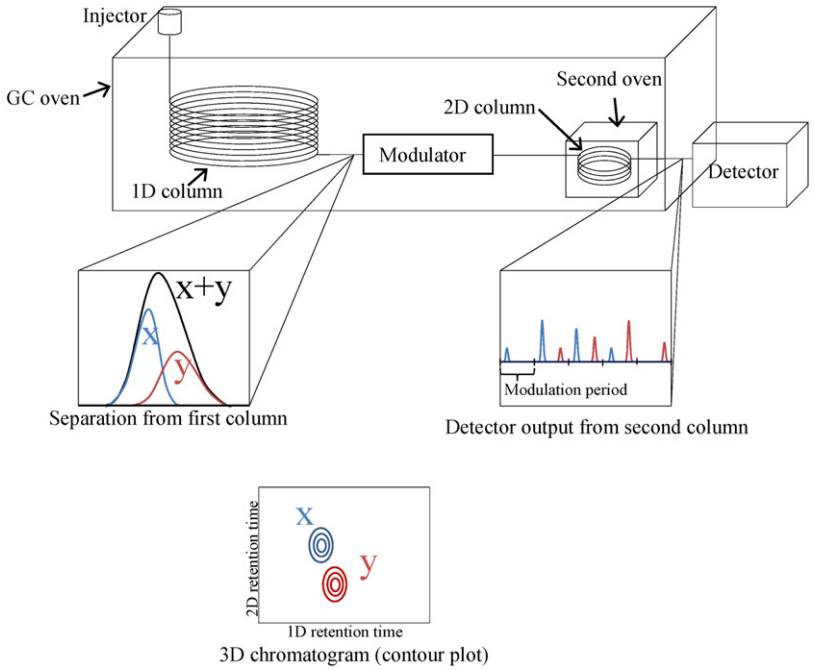

Fig. 1. Schematic of components of GC × GC and the separation after the first and second columns. After separation on the 1D column, analytes *x* and *y* are coeluting. The modulator takes small fractions from the first column and injects them into the second column where analytes *x* and *y* have different retentions. The detector records the modulated peaks eluting from the 2D column. The output from the detector is then processed into a 3D chromatogram (shown as a contour plot in the figure).

responsible for the three main advantages and to examine how these advantages are used in several different qualitative and quantitative approaches, including targeted and non-targeted analysis, group separations, and fingerprinting analysis. This review is not meant to be comprehensive, but rather to inform the reader of the types of analyses routinely performed in GC × GC and provide appropriate examples from the literature.

2. GC × GC advantages

2.1. Peak capacity

The rapid growth of GC × GC is in part due to the high resolution that the technique can potentially achieve. One of the advantages of GC × GC over traditional 1D GC is, in theory, it can provide a greater peak capacity. The peak capacity (n) is often used to describe the resolution of complex mixtures and is defined as the maximum number of adjacent separated peaks (at a specified resolution) that can fit in a given separation space [15]. As with all comprehensive 2D separations, the maximum peak capacity in GC × GC is the product of the peak capacity in each dimension as shown in Eq. (1)

$$n_{2D} = n_1 n_2 \quad (1)$$

where n_{2D} is the 2D peak capacity and n_1 and n_2 are the peak capacities in the first and second-dimensions, respectively [16]. Giddings intuitively described Eq. (1) by the formation of a grid that is defined by the peak capacity in each dimension, with each bin representing a peak which is schematically shown in Fig. 2 [17]. For a separation system to be considered as truly multidimensional and, hence, for Eq. (1) to describe the peak capacity, two requirements must be met. The first requirement is that the separations in the two or more dimensions must be orthogonal, i.e. independent of each other, and the second requirement is that the separations in both dimensions must be maintained throughout the entire separation process [17]. The first requirement in GC × GC can be met using two orthogonal columns in which the separation in the second dimension is not correlated with that of the first dimension. A more detailed discussion

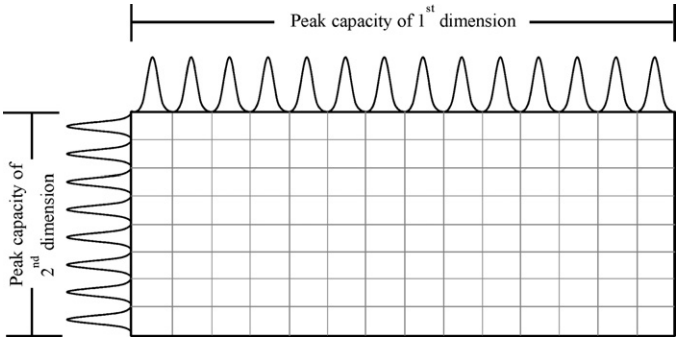

Fig. 2. Schematic showing the peak capacity of a 2D system in which the number of boxes is the multiple of the peak capacity in the 1st dimension and the peak capacity in the 2nd dimension.
Adapted from [17].

on orthogonal separations in GC × GC will be provided in Section 2.3. The second requirement is met in GC × GC through the modulator. The modulator takes small fractions from the first-dimension and injects them in a narrow band into the second-dimension. It has been determined that the first-dimension peak should be sampled at least three to four times to meet this second requirement [18,19].

Eq. (1) indicates that GC × GC can have high peak capacity, since it is the product of the peak capacities of the two columns. However, it should be noted that this is an approximation, and the peak capacity is in fact lower due to broadening in the second-dimension and peak reconstruction [17,20–22]. Blumberg et al. argued that although in theory GC × GC can provide a peak capacity up to a magnitude higher compared to 1D GC, under current instrumentation it does not perform better than an optimized 1D GC system because the injection pulses into the 2D are too wide [22]. In addition to the limitations of the current instrumentation, GC × GC is not usually run under optimal conditions. For example, the peaks in the first-dimension are often intentionally widened