Multidimensional gas chromatography

Philip J. Marriott, Sung-Tong Chin, Bussayarat Maikhunthod, Hans-Georg Schmarr, Stefan Bieri

Analytical multidimensional gas chromatography (MDGC) and the excellent separation efficiency it achieves serve advanced characterization of complex volatile and semi-volatile samples, which is unlikely to be accomplished by single-dimensional chromatography. Here, we provide a technical overview of recent method implementation in MDGC, for both the classical sense (i.e. conventional heart-cut MDGC), including recent approaches to MDGC, and the comprehensive two-dimensional gas chromatography (GC × GC) variant.

We summarize selected applications in diverse fields that best typify the role of these methods. We also draw attention to concepts (e.g., orthogonality of separation mechanisms and recently introduced microfluidic technology), and briefly comment on compatibility of detection systems.

As a guide to potential opportunities for continued innovation in multidimensional applications, we highlight the capabilities of GC platforms that either combine various GC × GC and MDGC arrangements or offer alternative operational modes for implementation of these methods.

Keywords: Comprehensive two-dimensional gas chromatography (GC × GC); Cryotrapping; Flow switching; Heart cut; High-resolution chromatography; Microfluidics; Multi-dimensional gas chromatography (MDGC); Multidimensional separation; Orthogonality; Volatile sample

Philip J. Marriott*, Sung-Tong Chin, Bussayarat Maikhunthod
Centre for Green Chemistry, School of Chemistry, Monash University, Wellington Rd, Clayton 3800, Australia

Hans-Georg Schmarr
Dienstleistungszentrum Ländlicher Raum (DLR) Rheinpfalz, Department Viticulture & Enology, Competence Centre Wine Research, Breitenweg 71, D-67435 Neustadt, Germany

Stefan Bieri
Official Food Control Authority of Geneva, 20 Quai Ernest Ansermet, 1211 Geneva, Switzerland

*Corresponding author.
Tel.: +61 3 99059630;
Fax: +61 3 99058501;
E-mail: Philip.Marriott@monash.edu

1. Definition of multidimensional gas chromatography

The present review uses the nomenclature and conventions proposed by Schoenmakers et al. [1], wherever possible. An all-encompassing definition of multidimensional chromatography (MDC) was promulgated by Giddings, who distinguished the two principal kinds of multidimensional systems as first, continuous two-dimensional (2D) operation (simultaneous zone displacement), and second, coupled column assemblies (sequential displacement) [2,3]. In an attempt to cover the current scope of 2D separations developed nowadays, Blumberg [4] recently proposed that MDC be redefined as ''*n*-dimensional analysis is one that generates *n*-dimensional displacement information''.

Since the first demonstration of multidimensional gas chromatography (MDGC) by Simmons and Snyder [5] in 1958, development of this separation technique paralleled trends evident in comparative one-dimensional (1D) technology (e.g., automated instrumentation, separation-phase improvement, and data analysis). However MDGC was differentiated by the interface and controls that enabled the coupling of the discrete dimensions. In particular, Marriott [6] defined MDGC analysis as ''the process of selecting a (limited) region or zone of eluted compounds issuing from the end of one GC column, and subsequently subjecting the zone to a further GC displacement''. None of these definitions implicitly stated that the separation of compounds would be improved by MDGC.

The potential and the principles of the MDGC technique have been outlined in various reviews [7–13], and it is not the purpose to review these further here apart from acknowledging that MDGC operation can involve several modes, namely packed-to-capillary separation, multiple heart-cutting to a secondary-dimension (^{2}D) column, multiple or parallel ^{2}D columns, multiple parallel traps, and multiple oven implementation [6], often with back-flushing of the primary dimension (^{1}D) column. A typical MDGC method focuses

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on a limited number of sampled ^{1}D regions, called heart-cuts (H/C) (hence it is often referred to as H/C MDGC), normally with a conventional dimension ^{2}D column, with the aim to improve separation. The sampled fractions have to be of small duration to prevent transferred peaks from overlapping on the ^{2}D column, so the classical single analytical column technique is unsuitable when many peaks are of interest and when they are scattered throughout the ^{1}D separation. For broad enhancement in resolution of all components in such a sample, many repeat injections must be made, with incremental shifting of the sampled ^{1}D zone, as described by Gordon et al. for tobacco essential oil [14].

An alternative MDGC approach – comprehensive 2D GC (GC × GC) – uses fast, continuous heart-cutting (modulation) with a sampling period less than the width of a ^{1}D peak for non-discriminative analysis [15]. Firmly established over the past decade [16–19], this is characterized by a short ^{2}D column, which ensures the required fast ^{2}D separations.

A procedure that is somewhat midway between these two approaches was recently reported as employing a slower sampling rate and collecting a broader elution zone from the ^{1}D column, and consequently can employ a longer ^{2}D column compared with that used in GC × GC [20].

The concept of multidimensionality in GC can be extended to combinations where conventional 1D chromatographic mechanisms are cross-coupled with a mass spectrometer (MS) capable of molecular separations when interfaced with a non-fragmenting ion source. Through adequate data treatment, such approaches produce comprehensive GC × MS contour plots with component-retention information *versus* (pseudo-) molecular ion mass (e.g., high-resolution MS) in an organized manner (compound-class separation), as first described by Wang et al. [21]. The potential and peak capacity of this complementary multidimensional separation, requiring no modulation device, has been compared with GC × GC [22,23].

Thus, GC × GC and MDGC have evolved into two mature, somewhat distinct, forms of multi-column GC. This fulfills the need to increase separation capability to resolve sample components requiring reporting at ever-decreasing levels for complex samples. The Chemical Abstracts Service database (with keywords ''multidimensional gas chromatography'' or ''two-dimensional gas chromatography'') shows significant growth in publication records in recent years (Fig. 1).

By reviewing the historical steps of both strategies and proposing innovative, versatile systems, we aim to spur further interest in these techniques and also to direct new opportunities in dimension expandability and comprehensiveness that arise by combining both approaches.

2. Comprehensive two-dimensional gas chromatography (GC × GC)

2.1. *Conceptual basis of GC × GC*

The approach to GC × GC was introduced and pioneered by Phillips et al. [15,24]. Today, it is widely accepted as

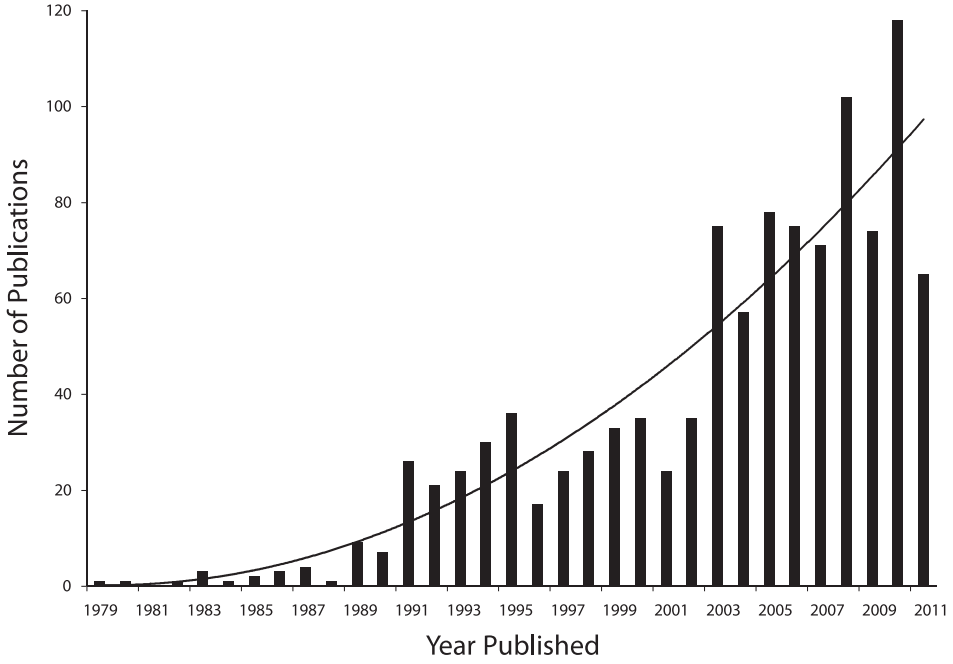

Figure 1. Number of publications per year that have been recorded in the Chemical Abstracts Service database with the keywords: multidimensional gas chromatography or two-dimensional gas chromatography, year 1979–2011 (accessed 17 June 2011).