Recent developments in comprehensive two-dimensional gas chromatography (GC × GC)☆ I. Introduction and instrumental set-up

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We review the literature on comprehensive two-dimensional gas chromatography (GC × GC), emphasizing developments in the period 2003–2005. The review opens with a general introduction, the principles of the technique and the set-up of GC × GC systems. It also discusses theoretical aspects, trends in instrumentation, column combinations, and detection techniques – notably mass spectrometric detection. We devote attention to a wide variety of applications and to analytical performance.

Keywords: Application; Complex sample; Comprehensive two-dimensional gas chromatography; Detection; GC × GC; Mass spectrometry; Modulation; Review

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1. Introduction

Some 15 years ago, comprehensive two-dimensional gas chromatography (GC × GC) began to attract attention and the full-colour 2D chromatogram of an oil sample published by John Phillips and his co-workers in 1991 [1] was an eye-opener for many analytical chemists. Over the years, quite a number of reviews on GC × GC have been published. Initially, they mainly discussed the principles of the technique and the basic theory – and, of course, the experimental set-up. Next, interfacing two GC columns became a key topic, and the first few applications were reported [2–6]. Most of these were in the field of petrochemical analysis and, for reasons which will be explained below, flame ionization detectors (FIDs) were invariably used for detection [7]. For an appreciation of the early developments, problems and (partial) solutions, the reader may consult reviews [8–10].

In the past few years, great steps forward have been made (e.g., in detection, analyte identification and quantification and, specifically, applications). Today, next to petrochemical analysis [11,12], areas such as food, air and environmental analysis are high on the list. This was nicely demonstrated in an extensive review [92] in which – next to technical developments – different types of application were highlighted. In this review, which covered the literature up to the end of 2002, close to 100 papers on GC × GC were quoted. It is somewhat unexpected to find, a mere three years later, that a further 150 papers discussing the new technique have been published. From amongst these, some 40 were published in J. Chromatogr., A 1019 (2003) and 1086 (2005), in special issues devoted to the First and Second International Symposium on Comprehensive Multidimensional Gas Chromatography held in Volendam (The Netherlands) and Atlanta (GA, USA), respectively. The steep increase underscores that GC × GC is, indeed, a rapidly emerging and increasingly successful technique. It therefore seems appropriate to discuss novel trends in instrumentation and techniques and to present a selected number of applications to indicate typical developments. While we intend the list of references to be exhaustive and we quote all published papers in at least one of the tables included in this paper, our emphasis

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Table 1. Main reviews devoted to GC × GC published in 2003–2005*

Year	Title	Number of refs.	Ref.
2003	Comprehensive two-dimensional gas chromatography: a powerful and versatile analytical tool	110	[92]
	Application of comprehensive two-dimensional gas chromatography to drugs analysis in doping control	55	[93]
	Comprehensive two-dimensional gas chromatography	19	[94]
	A review of environmental toxicant analysis by using multidimensional and comprehensive 2D-GC	90	[95]
	Opportunities for ultra-high resolution analysis of essential oils using comprehensive two-dimensional gas chromatography: a review	53	[96]
	Image background removal in comprehensive two-dimensional gas chromatography	3	[97]
2004	Information technologies for comprehensive two-dimensional gas chromatography	47	[98]
	The evolution of comprehensive two-dimensional chromatography (GC × GC)	86	[99]
	Trends in chemometric analysis of comprehensive two-dimensional separations	28	[100]
	Comprehensive two-dimensional chromatography in food analysis	83	[101]
	Comprehensive two-dimensional gas chromatography – a powerful and widely applicable technique	11	[102]
	Hyphenation of qMS to GC and GC × GC for the analysis of suspected allergens	19	[103]
2005	Comprehensive two-dimensional gas chromatography – a powerful and versatile technique	27	[104]

*Reviews briefly discussing GC × GC, but primarily treating related GC topics, have not been included.

will be on the period 2003–05. Table 1 summarizes the main review papers devoted to GC × GC in that period.

For the rest, we understand that quite a number of readers will not be familiar with the principles and basic instrumentation of GC × GC or terms such as 'modulation', 'wrap-around' and 'ordered structures', which are frequently used in this field. For their convenience, this review opens with an introductory section that should bring them up-to-date. More detailed information can be found elsewhere, especially [92].

2. Principles and instrumentation

2.1. General principles

Since its early days, GC has been recognized as a tool offering higher peak capacities than other chromatographic techniques. Over the years, dramatic progress has been made and, today, state-of-the-art one-dimensional (1D) GC on capillary columns can, typically, separate some 100–150 peaks in one run. However, this does not suffice to separate the individual constituents of many different types of sample, ranging from oils or petrochemical products to contaminated fish and food, cigarette smoke and polluted air, and technical mixtures of polychlorinated biphenyls or toxaphene.

One way to improve the separation power of a GC system effectively is to couple, through an interface, two independent columns. The superiority of such two-dimensional (2D) GC over 1D-GC was demonstrated for a capillary-column system some 40 years ago [271] and, over the years, so-called multidimensional gas chromatography, abbreviated as MDGC or GC–GC, has been successfully applied to a variety of problems [271,273,274]. Illustrative examples [272] indicate the limitation of the approach. In the large majority of cases, the applications are of the heart-cutting type: only one, or a few, narrow fraction(s) of the eluate from the first column is/are transported to the second column for further separation. In other words, the technique can be recommended, and is very successful, if information is required about only a few fractions that contain all analytes of interest – typically a target-analysis situation.

However, whenever screening of an entire sample is the main aim (i.e. when unknowns play a major role), MDGC rapidly becomes an extremely laborious and time-consuming technique, with very careful fractionation, lengthy re-analysis of all fractions, and reconstruction of the chromatograms as the major problems. It will be clear that one cannot find a way out by increasing the width of the first-column fractions: using wider fractions will simply destroy more of the first-column resolution.

The alternative is to subject the sample to a comprehensive 2D-GC separation: rather than being separated into a few fractions, the entire sample is now separated on two different columns, the fractions are kept narrow to ensure that no information gained during the first separation is lost and – certainly in GC as opposed to liquid chromatography (LC) – the instrumental set-up is constructed so as to ensure that the total 2D separation is completed within the run time of the first-dimension analysis. In other words, compared with MDGC, GC × GC promises to yield substantially improved resolution for all sample constituents with no loss of time [105,106].

The schematic of a GC × GC system is shown in Scheme 1 (adapted from [92]). Typically, two GC separations based on distinctly different separation mechanisms are used, with the interface – called a modulator (see Section 2.3, Part II) – between them. Its main functions are to cut and to refocus narrow adjacent fractions