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Two-Dimensional Gas Chromatography

GCxGC is truly a hyphenated technique in the sense that the entire sample passing through the first column also passes through the second column

From: Fire Debris Analysis, 2008

Related terms:

Solid-Phase Microextraction, Modulator, Metabolite, Volatile Organic Compound, Chromatography, Time-of-Flight Mass Spectrometry, Gas Chromatography Mass Spectrometry (GCMS)

Organic Geochemistry

K. Grice, C. Eiserbeck, in Treatise on Geochemistry (Second Edition), 2014

12.3.6.5 Comprehensive Two-Dimensional Gas Chromatography (GCxGC)

GCxGC has become a revolutionary tool capable of high-resolution separation of biomarkers in complex mixtures (e.g., Dimandja, 2004; Eiserbeck et al., 2011, 2012; Merritt and Hayes, 1994; Ventura et al., 2007). GCxGC meets the visualization of 2D analytical separation anticipated some 25 years ago (Giddings, 1984). The resolution power of GCxGC has been established based on linking two GC columns consisting of different stationary phases, for example, nonpolar and polar connected via a cryogenic dual-stage modulator to concentrate the fraction eluting from the first GC column within a certain modulation period to a fine band. This fraction is then injected into a second GC column where it is separated based on the different chromatographic selectivity (Adahchour et al., 2008). The technique is regarded as comprehensive since all the fraction collected from the first column is then transferred to a second separation dimension. This technique differs from other multidimensional techniques, for example, heart-cut (e.g., Sciarrone et al., 2010), which only transfers specific fractions of the sample for further separation. The addition of the second dimension enhances the peak capacity of a chromatogram by 20-fold as all compounds in a sample can be distributed within an area spanned by the first and second dimension rather than only in the one dimension.

A coupling of this separation technique with compound-specific isotope measurements would add a whole new dimension to isotope geochemistry. First steps have been taken toward such a system (Tobias et al., 2011). Further improvements of this tool promise a much broader application of isotope geochemistry.

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URL: https://www.sciencedirect.com/science/article/pii/B9780080959757010068

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Other Techniques of Analysis and the Future of Fire Debris Analysis

Eric Stauffer, ... Reta Newman, in Fire Debris Analysis, 2008

13.2.4 Final Comments

GCxGC–TOFMS offers an extremely promising future in the field of fire debris analysis. It permits better separation, and, therefore, better specificity of the analysis of ILR. Validation studies are currently in progress, and once they are completed and the cost of benchtop time-of-flight mass spectrometers and comprehensive two-dimensional chromatographic systems decreases, it is likely that more people will use this kind of instrument. This will be the change of technique that will lead to a significant improvement of the analysis of fire debris samples in the future.

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Analysis of Cannabis

Elizabeth M. Humston-Fulmer, ... Joseph E. Binkley, in Comprehensive Analytical Chemistry, 2020

2.3 Multidimensional chromatography

Comprehensive two-dimensional GC (GCxGC) extends the chromatographic separation by pairing two columns with complementary stationary phases. Since chromatographic separations are based on analyte interactions with the stationary phase, GCxGC takes advantage of the fact that analyte interactions differ depending on the properties of the phase. Analytes that coelute with one type of stationary phase do not necessarily coelute on a different type of stationary phase, for example. The concept of GCxGC is to pair columns with complementary stationary phases in series so that each sample is separated by both separation mechanisms at essentially the same time [18]. Analytes may coelute on one phase or the other, but fewer will coelute on both. As diagramed in Fig. 5, the heart of GCxGC is a modulating device that connects the primary column to the secondary column. The modulator also collects the primary column effluent, refocuses the effluent, and reinjects it to the second dimension column. This is performed with a frequency that balances maintaining the primary column separation with sufficiently resolving analytes on the complementary stationary phase in the short second separation dimension. Careful consideration of detector is also crucial as the peak widths from the second dimension separation are expected to be much narrower than is typical with one-dimensional GC. Because of its fast acquisition rate capabilities, TOFMS is ideal for proper delineation of these narrow second dimension peaks. Commercially available hardware and method development software tools [19] have the capacity to make this type of analysis routine.

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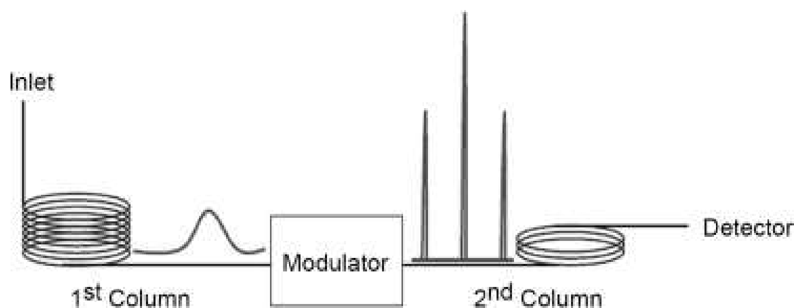

Fig. 5. Instrument schematic of GCxGC showing effluent peak from primary separation, modulator, and narrower peaks in the second dimension separation.

A GCxGC separation of the cannabis sample shown in Fig. 1A is shown in Fig. 6. The method details for the GCxGC separation are provided in Section 4, but the primary column separation conditions were maintained with both analyses. The retention times in the first dimension are consistent and analytes from the GC separation can be visually connected to those in the GCxGC separation by matching first dimension retention times. For example, CBD and α-pinene, shown in Figs. 1 and 2, are also indicated on the plots in Fig. 6. GCxGC effectively spreads the analytes out into two-dimensional space, as demonstrated with this top-down contour plot, shown with log colour scale.

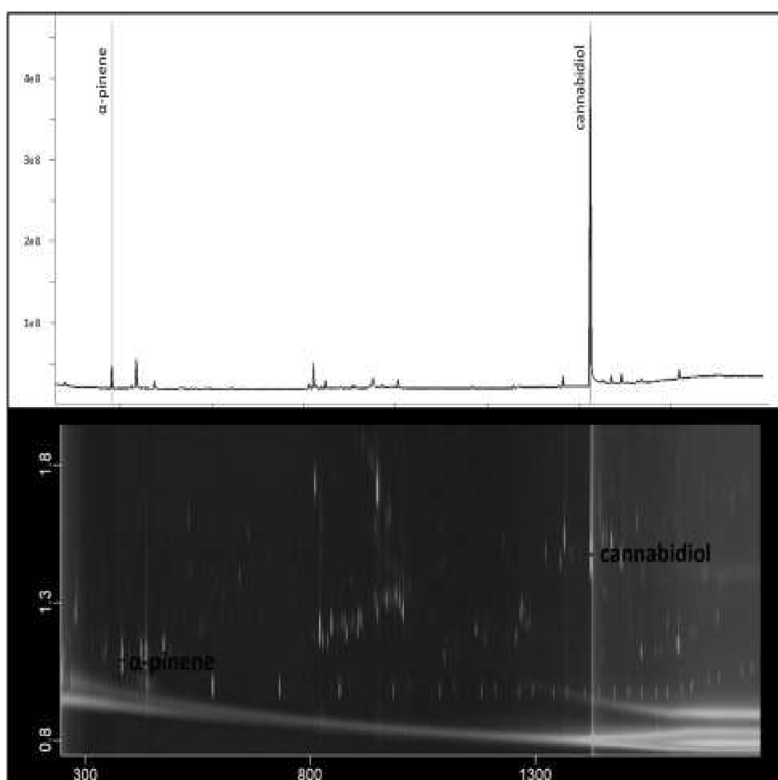

Fig. 6. The Type III cannabis sample shown in Fig. 1 was also analysed with GCxGC. CBD and α-pinene are indicated.

One of the most often discussed benefits of GCxGC is the increase in peak capacity, which allows for separating more analytes in chromatographic space. For example, a GCxGC separation of the coelution that required deconvolution in Fig. 4 is shown in Fig. 7. Butyrolactone and ethyl pyrazine have similar retention index values for the primary separation (a semi-standard non polar column), but have different retention index values on a polar column (1632 and 1337, respectively), which was used for the second dimension separation. When separated with both mechanisms in GCxGC, what had required deconvolution to separate in one dimension is chromatographically resolved in the second. Analytes that are vertically aligned in the contour plot in Fig. 6 are other examples of coelutions in GC separation that have benefitted from this increase in peak capacity.

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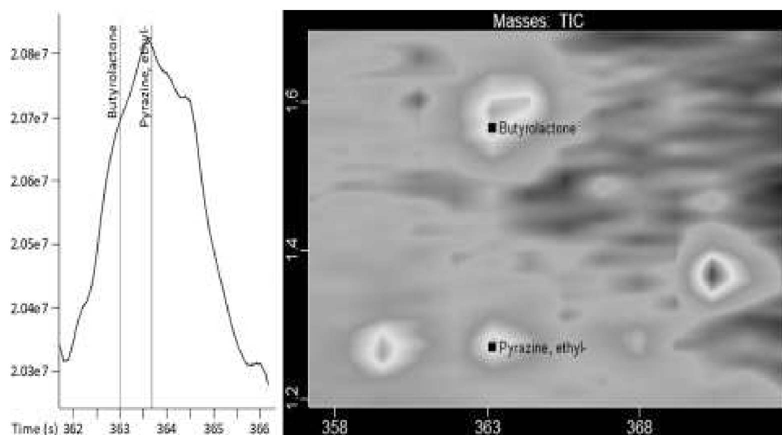

Fig. 7. The coelution that required deconvolution (left, also shown in Fig. 4) chromatographically separates in the second dimension with GCxGC (right).

This benefit is even more important when the additional peak capacity is able to separate compounds that were not efficiently deconvoluted in the GC data. For example, an apparent single peak from the GC-TOFMS data that was not reliably identified is shown in Fig. 8. The best library match for this analyte was a monoterpene, bicyco[2.1.1.]hexane, 5,5-dimethyl-1-vinyl with a similarity score of 767. While retention index supported this identification (observed = 923 and library = 921), there are notable discrepancies in the spectral information. Both *m*/*z* 67.06 and 108.07 are present higher than the expected ratios in the observed data. These discrepancies would have mostly likely left this analyte an unknown if additional targeted experimentation were not performed. However, the GCxGC data shown in Fig. 8 reveals that a perfect first dimension coelution of 2,3-dimethyl pyrazine was overlapped with the terpene. The spectrum observed from the GC separation that did not match well to library databases is the merged spectra of these two coeluting analytes. With GCxGC and chromatographic separation in the second dimension, the similarity score for the terpene improved to 914 and the previously not found compound matched to 2,3-dimethyl pyrazine with a similarity score of 862. Retention index information further supported the identification of the newly detected pyrazine compound (observed = 922 and library = 926). In this case, GCxGC was able to turn one unreliably identified analyte into two analytes with confident identifications, improving the chemical understanding of this cannabis sample.

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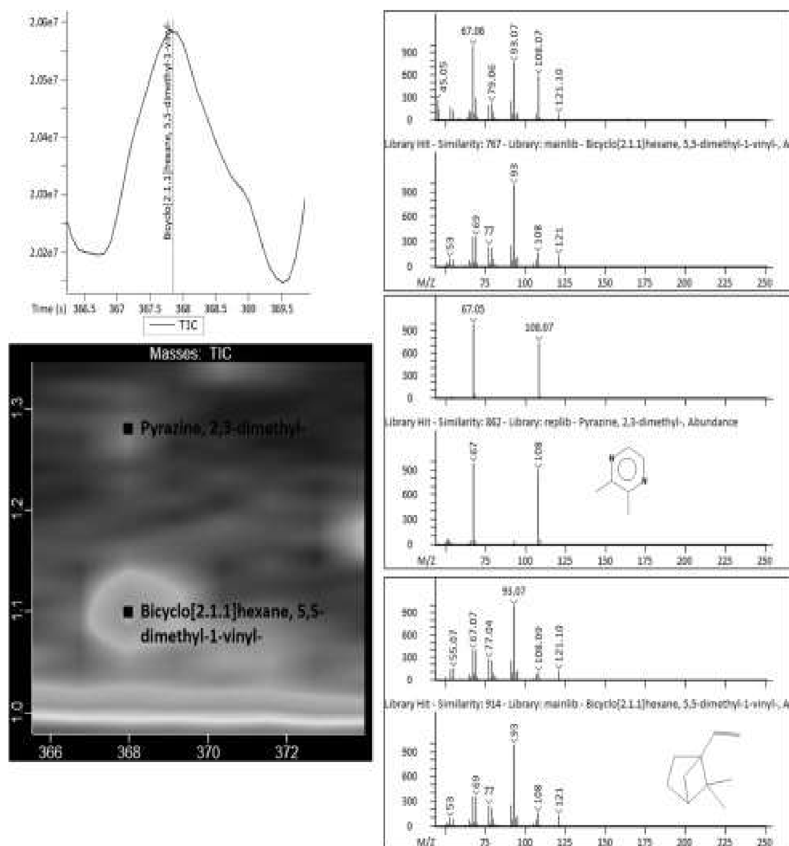

Fig. 8. A coelution that exceeds deconvolution with GC (top) is separated in the second dimension with GCxGC (bottom).

The increased peak capacity and TOFMS detection improves sample characterization by providing additional analyte information. GCxGC further improves characterization by also producing structured chromatograms. Because there is some consistency in the types of interactions that analytes with the same functional groups have with each stationary phase, analytes of the same compound class tend to elute in structured bands across the GCxGC separation space, as demonstrated in Fig. 9. For example, bands of terpenes (monoterpenes and sesquiterpenes), terpenoids (monoterpenoids and sesquiterpenoids), and cannabinoids are all readily apparent in the contour plot displayed below. This aspect of GCxGC provides better visual characterization of a sample and leads to improved chemical profiling.

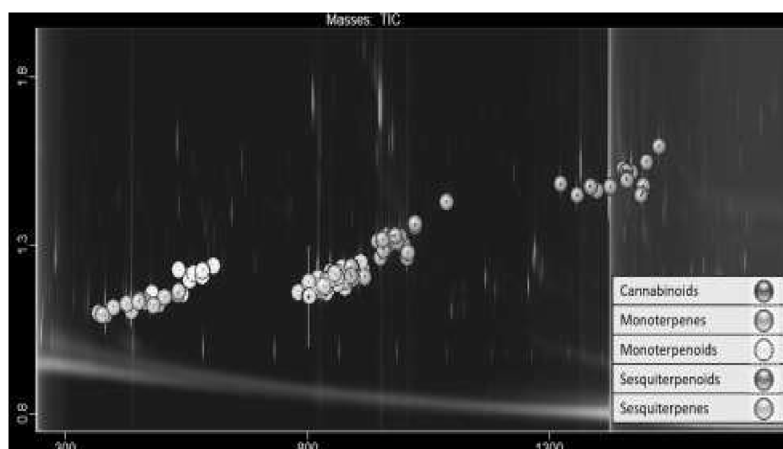

Fig. 9. Structured bands through the GCxGC separation space highlight compound classes of interest.

The combined analytical capabilities of GCxGC-TOFMS leads to additional analyte information for better characterization of complex samples, which facilitates

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improved differentiation of cannabis samples and chemovar classifications, as described in the next section.

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Basic Multidimensional Gas Chromatography

Pierre-Hugues Stefanuto, Jean-François Focant, in Separation Science and Technology, 2020

Abstract

Two-dimensional gas chromatography (GC×GC) is a powerful separation technique, allowing to reach unique separation resolution. GC×GC is thus well suited for the characterization of complex volatile and semi-volatile mixtures. This high peak capacity results from the addition of an extra GC dimension. GC×GC can further offer structured separations into the available 2D chromatographic space, supporting compound classification. Obtaining the best out of a GC×GC separation however requires a serious and expert-dependent optimization of the analytical parameters.On the hardware side, a GC×GC system is highly similar to a GC system. The addition of a second column and an interface (a modulator) between the two columns are the only addition. In addition to the general optimization of chromatographic parameters, the efficiency of the separation strongly relies on the column combinations and modulation parameters. Currently, the selection of the column set as well as the fine tuning of most analytical parameters relies mainly on user's experience and empirical development that can miss latest developments in column technologies. The resulting optimization workflow can be time consuming and often conduct to not fully optimal methods. A comprehensive method optimization is becoming more and more complex and new workflows are required.Nowadays, this field is ongoing a paradigm shift. With the continuous development of model-based separation simulation, there is growing interest on in silico method optimization. In the future, the capacity to predict the optimal analytical conditions would make complex techniques, such as GC×GC, more accessible by decreasing the time and expertise required for the development and optimization.

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Comprehensive Gas Chromatography Methodologies for the Analysis of Lipids

Giorgia Purcaro, ... Luigi Mondello, in Handbook of Advanced Chromatography/Mass Spectrometry Techniques, 2017

Abstract

Comprehensive two-dimensional gas chromatography (GC × GC) is a powerful analytical tool when dealing with complex mixtures and it has been increasingly and successfully employed in various applications over the last two decades. In GC × GC, every part of the sample is subject to two individual separation dimensions resulting in a tremendous increase in resolving power when orthogonal separation mechanisms are combined. In this chapter, an overview of the state of the art of this technique, with emphasis on applications developed in the lipid field, is provided. Fatty acid methyl esters have been the most exploited

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application, but more recently attention has been moved to other lipid components, such as sterols, waxes, and the entire unsaponifiable fraction. Furthermore, GC × GC can be a valuable tool to study the volatile fraction of high-value oils, in particular olive oil, for authenticity and quality assessment.

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URL: https://www.sciencedirect.com/science/article/pii/B978012811732300011X

Analytical Methods to Determine Potentially Allergenic Fragrance-Related Substances in Cosmetics

A. Chaintreau, in Analysis of Cosmetic Products, 2007

Comprehensive two-dimensional gas chromatography

Comprehensive two-dimensional gas chromatography (GC×GC) is a recent technique, proposed in the 90s by Philips (Liu and Phillips, 1991). Analytes eluting from a first and classical capillary column are re-focused (e.g. in a cryo trap as shown in Figure 6.2.3) and periodically transferred into a second, fast-GC column to be further separated, which requires a high sampling rate detector. In practice, this technique is like a MDGC, where the heart-cut and re-injection in the second column would be constantly repeated (every 2–5 s) along the whole chromatogram. In contrast to MDGC, there is no need to target the analytes in question or to adjust the time windows accordingly, as the first chromatogram is permanently “sliced”.

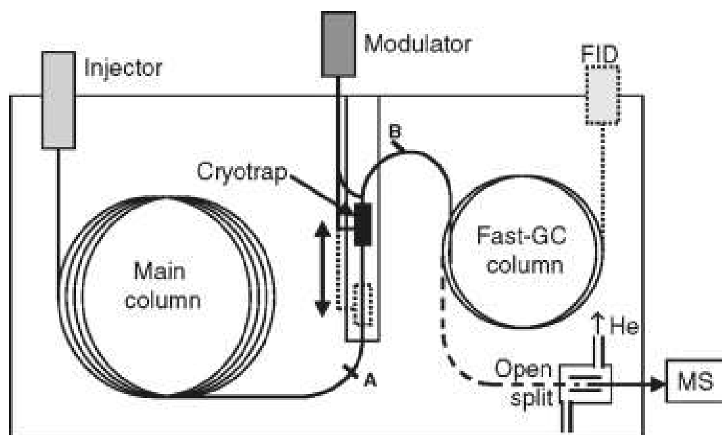

Figure 6.2.3. Comprehensive gas chromatography with either MS (long dotted line) or FID (short dotted line) detection and using a longitudinally modulated cryogenic system.

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A priori, the overall peak capacity of GCXGC is the product of peak capacities of both columns. But, in fact, the peak capacity of the first column can only be multiplied by up to 10 (Blumberg, 2003), which, in any event, greatly exceeds the abilities of any other GC technique. A detailed description of the technique can be found in various reviews (Ong and Marriott, 2002; Shellie and Marriott, 2003).

Chromatograms resulting from a GC×GC analysis can be represented as three-dimensional figures (Figure 6.2.4 (left)). The virtual chromatogram along the first axis (^{1}D) (Figure 6.2.4 (left), in red) indicates what would be observed with a monodimensional GC. As fractions of this virtual chromatogram are periodically re-injected in the second column after each modulation of the cold trap, a series of brief chromatograms is obtained (Figure 6.2.4 (left), blue lines). If the peak width in the first dimension exceeds the modulation period, the corresponding peak may appear in several modulations. Therefore, peaks belonging to a same compound

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are grouped (green cycles) and chromatograms are usually represented in two-dimensions as "contour plots" (Figure 6.2.4 (right)) where peak intensity is coded by appropriate colors within a spot and then integrated using a dedicated software.

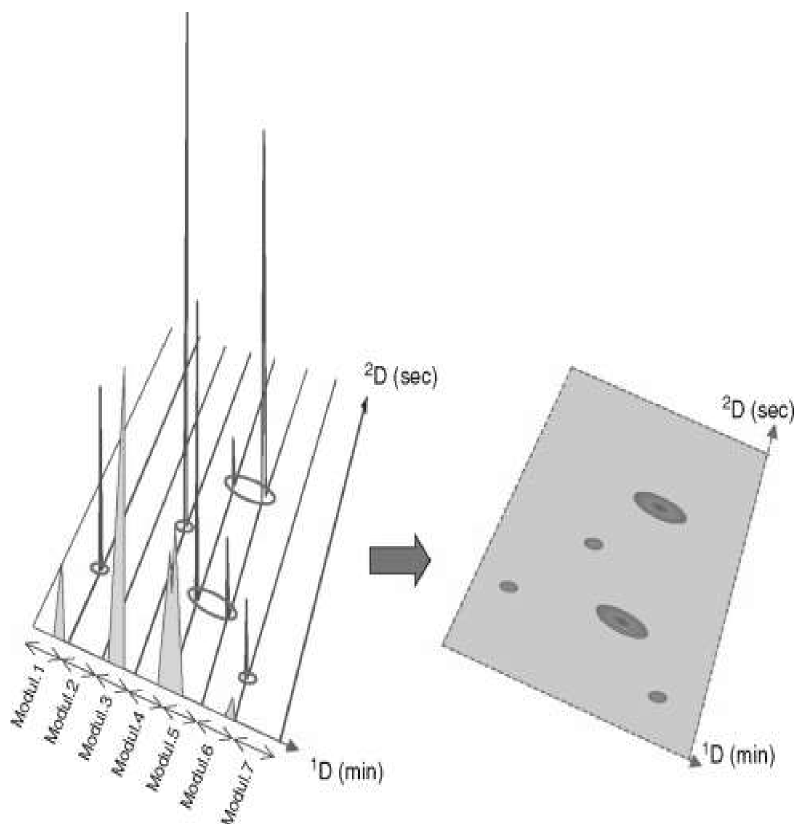

Figure 6.2.4. Principle of three- and two-dimensional representations of GC×GC chromatograms.

Two configurations have been tested for PASs determination. First an FID was used by Shellie *et al.* (2004) but, as shown in Table 6.2.4, it did not perform better than a GC-MS for a complex sample. This was presumably due to the fact that GCX GC-FID and GC-MS are both two-dimensional techniques, which seems to be insufficient for the resolution of most complex co-elutions. Therefore, coupling GC×GC to MS, would become a powerful tool. Thus, in another paper by the same group (Debonneville and Chaintreau, 2004) a quadrupole MS in EI ionization mode was used as a detector (see Figure 6.2.3). However, as mentioned above, the short and narrow column of the second dimension is operated in fast mode and requires a high sampling rate, which does not make quadrupole an ideal candidate as a GC×GC detector. In spite of its low sampling rate, good quantitative performances were observed when only one ion was monitored separately, as can be seen in Table 6.2.4. The resulting 2-D chromatogram (Figure 6.2.5) shows that the target analytes were clearly separated from any other peak. However, these experiments were done using a prototype hyphenation between a quadrupole MS and a GC×GC chromatograph, which is not yet commercially available.

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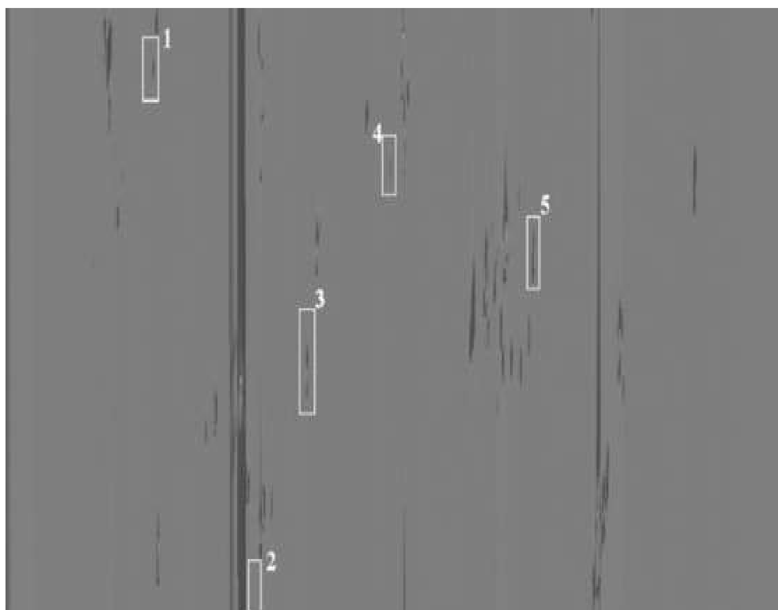

Figure 6.2.5. Contour-plot resulting from the GC×GC-MS(EI) analysis of a PAS-free fragrance concentrate containing 168 constituents spiked with five PASs at a level of 50 mg/L. (1) Linalool, (2) anise alcohol, (3) eugenol, (4) alpha-isomethyl ionone, and (5) benzyl benzoate.

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The use of GC×GC hyphenated to a time-of-flight MS (TOF-MS) detector, which provides a higher sampling rate than quadrupole, has also been reported (LECO, 2004). It offers the unrivalled advantage of allowing quantification and identification of peaks with full scan unlike the aforementioned approach. However, despite the great increase in peak resolution obtained, coelutions of target peaks with matrix peaks can still be present, which makes it necessary to apply mathematical approaches, such as peak deconvolution. However, some problems of quantification accuracy persist, such as a lack of linearity of calibration lines (LECO, 2004) and last, but not least, the cost and complexity of such instruments are not suitable for quality control.

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Advanced Techniques in Gas Chromatography–Mass Spectrometry (GC–MS–MS and GC–TOF–MS) for Environmental Chemistry

Jeffrey R. Gilbert, ... Paul Lewer, in Comprehensive Analytical Chemistry, 2013

3.1 Comprehensive Two-Dimensional Gas Chromatography Time-of-Flight Mass Spectrometry (GC × GC–TOF-MS)

Comprehensive two-dimensional gas chromatography (GC × GC) was first demonstrated by John Phillips in 1991 [33]. For the first 9–10 years, it was practiced by only a select few research groups. In 1998, cryogenic modulation was introduced [34], which set the stage for reliable focusing of effluent from the first-dimension column into extremely narrow peaks (60 ms) for release onto the second-dimension column. The narrow peak widths necessitated using a time-of-flight mass spectrometer to maintain the mass spectral and chromatographic fidelity of the two-dimensional chromatograms. In 2001, LECO introduced the Pegasus 4D GC × GC–TOF-MS, which became the industry standard for the next 10 years. The majority of GC × GC publications cites the use of this instrument,

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and thus it has been largely responsible for the growth of GC × GC as a tool for the separation of complex mixtures. In 2002, Dalluge *et al*. published the first articles demonstrating the sensitivity and resolving power of GC × GC–TOF-MS [35–37]. Since that time, there have been nearly 700 publications in this field. These have been reviewed by Gorecki, Cortes, and Meinert [38–41].

GC × GC separations using cryogenic modulation are well suited for coupling to a mass spectrometer because the flow rate exiting the second-dimension column is typically 1 ml/min. Commonly, a 0.25 mm ID capillary column is used in the first dimension, and a 0.1 mm ID column with a length of 1–1.5 m is used in the second dimension. A minor consequence of this coupling is retention time shift due to the flow profile along the length of the first-dimension column being flatter than if it were coupled directly to vacuum at the outlet. A more significant consideration is that components at high concentrations can easily overload the second-dimension column. This is apparent in the two-dimensional plots as vertical streaks, making it impossible to detect components that coelute in the first dimension. To address this issue, some researchers have started using second-dimension columns with either 0.18 mm or 0.25 mm ID to provide greater sample capacity.

Alternatives to a conventional TOF-MS have been demonstrated with a supersonic beam MS developed by Amirav coupled with fast-scanning quadrupole mass spectrometers [42]. The former is ideally suited for flow modulation, developed by Seeley, where the flow from the second-dimension column is 20–30 ml/min. [43–45]. Fast-scanning quadrupole mass spectrometers, operated at 20–50 scans/s, do reasonably well at producing spectra that match library spectra [46]. Thus far, CI has not been applied in published research, which may result from the fact that the open source design of the LECO Pegasus 4D is not well suited for CI.

One of the biggest opportunities for the advancement of GC × GC–TOF-MS is in handling the data produced by the experiments. The number of components observed by a single GC × GC–TOF-MS analysis can be easily 5000–10,000 and, as a consequence, a typical unit resolution data file run with a TOF-MS is over 1 GB in size. This is due to both increased sensitivity and resolution compared with 1D GC–TOF-MS. Data files will become even larger for high-resolution TOF-MS analysis, and tools for analyzing complex data sets are still evolving. However, both LECO and Zoex currently have software that can facilitate the comparison of data files to identify the key differences.

In one example of the use of GC × GC–TOF-MS, polyacrylic acid was pyrolyzed, and the products were analyzed with the results shown in Figure 9. The sensitivity of the TOF-MS combined with the sensitivity gain using GC × GC revealed more components than previously reported by 1D GC, and also showed a number of unresolved components present in the first dimension. Some of these 1D resolution problems could be solved by peak deconvolution, but could not provide the same recognition of differences in chemical functionality that was readily seen in the 2D GC × GC plot.

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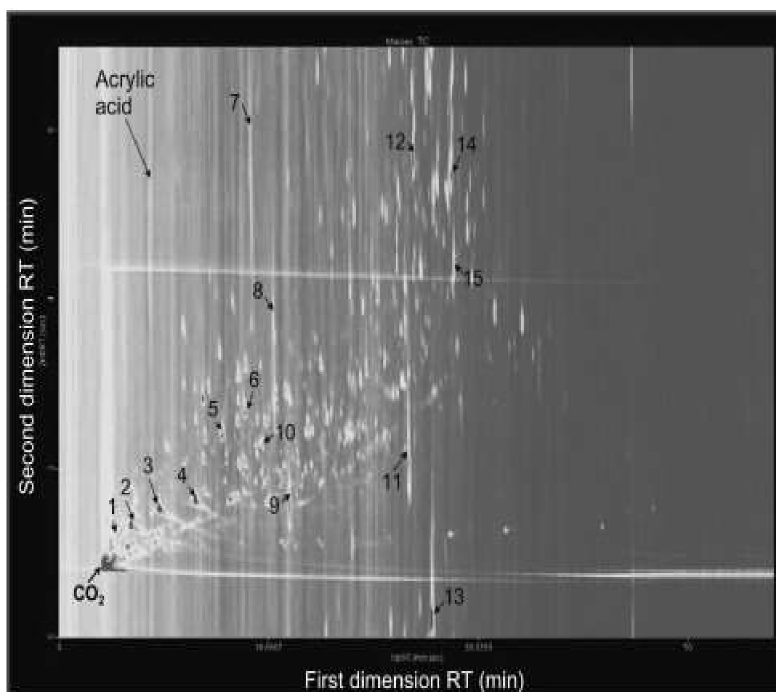

Figure 9. Pyrolysis GC × GC–TOF-MS of poly(acrylic acid). Component ID's 1, methacrylic aldehyde; 2, benzene; 3, toluene; 4, xylene; 5, 3-methyl-3-cyclohexen-1-one; 6, 3-methyl-2-cyclohexen-1-one; 7, phenol; 8, methyl phenol; 9, dimethyl phenol; 10, 2-3,5-dimethyl-cyclohexen-1-one; 11, MW 146; 12, MW 162; 13, MW 160; 14, MW 174; 15, MW 178.

For samples of complex mixtures that have many homologues, patterns may appear in the reconstructed GC × GC plots that aid in the interpretation of the sample composition. In this way, GC × GC is complementary to MS, as it reveals differences in chemical structure for components that are isobaric. Figure 10 illustrates a second example of the use of GC × GC–TOF-MS for the separation of diesel fuel, where a nonpolar column was used in the first dimension and a polar column was used in the second dimension. Regions of differing chemical functionality are labeled in the figure, which demonstrates that such a sample comprises several chemical families that are superimposed in the first dimension of separation. Even with this GC × GC separation, not all components are completely resolved. To provide improved separation for paraffins and olefins, the phase sequence can be reversed, with the polar phase in the first dimension and the nonpolar phase in the second dimension.

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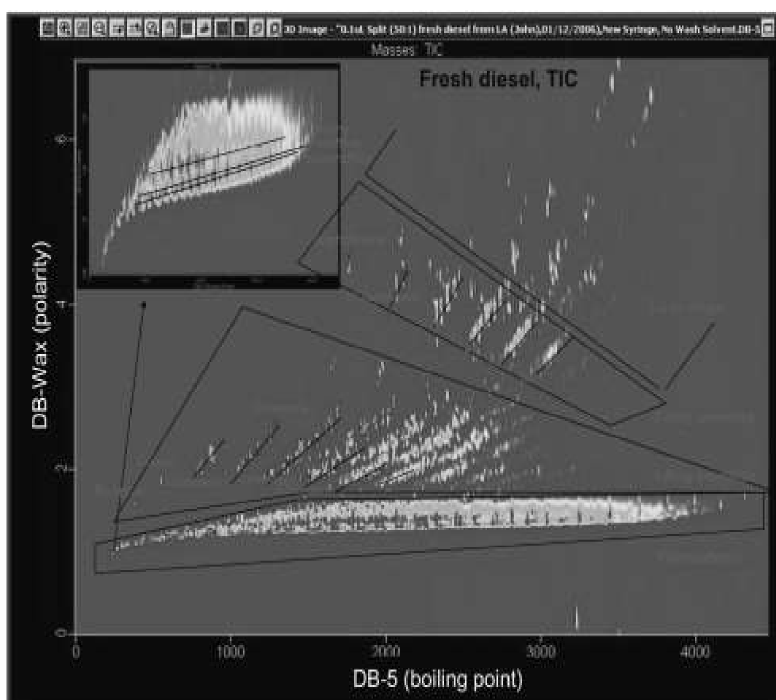

Figure 10. GC × GC–TOF-MS profile of diesel fuel, illustrating the complementary nature of separation of isobaric compounds using GC × GC and mass spectra.

In summary, GC × GC–TOF-MS has been in general use for over 10 years, but it is far from mature as an experimental technique. The introduction of high-resolution mass spectrometers and CI is spawning a fresh wave of application development. GC × GC is complementary to MS in the information that it provides, especially in the case of isomers where the mass spectra do not provide sufficient differentiation for identification. Thus far, little has been done to explore the relationships of two-dimensional retention times and quantitative structure property relationships. There is incredible opportunity to further explore the rich data sets that are produced by GC × GC–TOF-MS. This will continue to drive the development of advanced data evaluation tools.

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Basic Multidimensional Gas Chromatography

Nicholas H. Snow, in Separation Science and Technology, 2020

8.7 Forensic and toxicology

Forensic applications of GCxGC have been recently reviewed by Sampat et al. and Gruber et al. [16,17] While applications in forensic science have not been as rapid to evolve, GCxGC and GCxGC-MS have great potential as tools in forensic and toxicological analysis. Sampat et al. separate forensic applications of GCxGC into several main areas, including illicit drugs, forensic toxicology, fire debris, fossil analysis, environmental investigations, and explosives. Gruber et al. discuss the rapid extension of these topics in human scent analysis, arson, security, and environmental investigations. As with all new techniques, adoption in forensics and toxicology is slow due to legal and evidentiary requirements.

Mitrevski, Wynne, and Marriott provided an excellent discussion and comparison of one- and two-dimensional gas chromatographic analysis of several illicit drug classes [18]. Fig. 8.8 shows both the one-dimensional and two-dimensional chromatograms for the analysis of a heroin sample. Note the numerous overlapping peaks and baseline drift in the one-dimensional chromatogram. The

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two-dimensional chromatogram shows most of the peaks along the diagonal, indicating a highly correlated separation. In this case, the main benefit of the two-dimensional separation was stated as an increased signal to noise ratio. Also, note the small regularly spaced peaks at the bottom of the two-dimensional chromatogram. These are likely caused by a small amount of septum bleed. Note that even in this highly correlated separation, analytes are separated from such interferences.

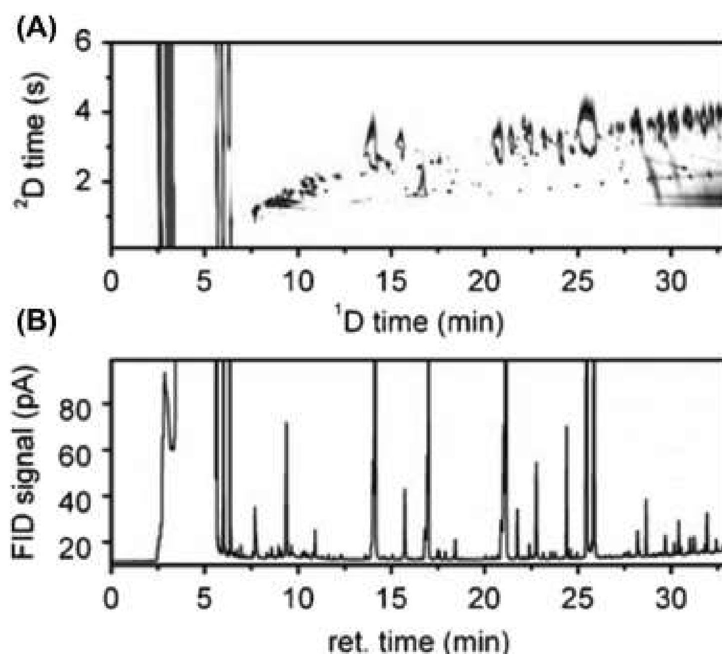

Figure 8.8. Heroin impurity profile analyzed in GCxGC-FID mode (A) and in 1D GC-FID mode (B). The BPX5/BPX50 column set was used in GCxGC, and the same D column (BPX5) was used in 1D GC-FID.

Reprinted with permission from B. Mitrevski, P. Wynne, P.J. Marriott, Comprehensive two-dimensional gas chromatography applied to illicit drug analysis, Anal. Bioanal. Chem. 401 (2011) 2361–2371, https://doi.org/10.1007/s00216-011-5234-6. Copyright 2011, Springer.

Table 8.4 shows a list of forensic and toxicology applications discussed in this text. From almost the beginning of the commercial availability of GCxGC, there has been an interest in breath analysis for both forensic and toxicological analysis. Additional application examples include drugs in urine and study of training aids for drug and bomb-sniffing dogs.

Table 8.4. Forensic and Toxicology applications discussed in this text.

Chapter	Reference	Year	Analyte/Sample
5	202	2006	Volatile organic compounds in human breath
5	203	2006	Human breath
5	85	2010	Drug analysis of hair extracts
5	206	2010	Breath gas analysis in the clinical environment
3	47	2012	Synthetic canine training aids
5	52	2012	Salvinorin A in plants, water, and urine
5	84	2014	Multiple steroidal compounds in synthetic urine
5	160	2015	Cadaveric decomposition odor analysis

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Chapter	Reference	Year	Analyte/Sample
5	161	2015	Explosive profiling
5	162	2015	Decomposition volatile organic compounds in soil
5	163	2015	Carrion volatiles in decomposition soil
5	83	2016	Endogenous anabolic steroid in urine
7	60	2016	Vacuum ultraviolet absorption spectroscopy in combination with comprehensive two-dimensional gas chromatography for the monitoring of volatile organic compounds in breath: a feasibility study
5	165	2017	Textiles associated with decomposing remains
5	167	2017	Human odor and forensics
5	166	2018	Scent of weathered training aids for blood-detection dogs
5	204	2018	Volatile biomarkers of therapeutic radiation in breath
3, 5	8, 200	2018	Critical review of recent trends
3	48	2019	Breath analysis within a large-scale clinical study

The analysis of breath gases has been of interest in GCxGC since nearly its inception. Recently, Gruber and colleagues combined GCxGC with a relatively new detector, vacuum ultraviolet spectrometry (VUV) to generate an additional layer of selectivity that is complementary to classical MS [19]. They analyzed VOCs in breath using GCxGC-VUV to demonstrate the potential for GCxGC-VUV in health monitoring using breath. Fig. 8.9 shows both the chromatograms and VUV spectra of several VOCs in breath. While limits of detection are higher with VUV detection than observed with ToFMS detection, VUV detection limits are adequate for many clinical and health monitoring applications; they used a glucose challenge to demonstrate the feasibility of VUV as a detector for breath gas analysis.

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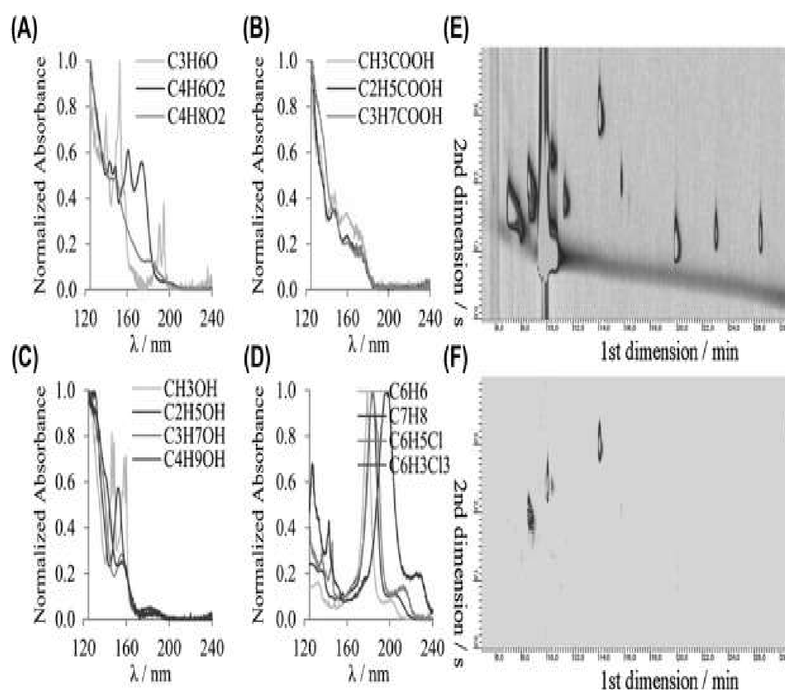

Figure 8.9. VUV spectra and two-dimensional chromatogram showing separation and identification of breath gases. A, B, C, D: VUV spectra of the indicated analytes; E: GC×GC-VUV chromatogram of humid gas standard (full range 120–240 nm); F: GC×GC-VUV chromatogram of humid gas standard (limited range 170–200 nm).

Reprinted with permission from B. Gruber, T. Gröger, D. Harrison, R. Zimmermann, Vacuum ultraviolet absorption spectroscopy in combination with comprehensive two-dimensional gas chromatography for the monitoring of volatile organic compounds in breath gas: A feasibility study, J. Chromatogr. A. 1464 (2016) 141–146. Copyright 2016 Elsevier Science.

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Classical two-dimensional GC combined with mass spectrometry

Frank David, in Hyphenations of Capillary Chromatography with Mass Spectrometry, 2020

2.1.1.1 Introduction and history

The history of two-dimensional gas chromatography (2D-GC), whereby fractions of a sample are separated on two different GC columns, dates back to the same decade as the first publication on gas-liquid chromatography by James and Martin [1]. The first application of two-dimensional gas chromatography, published by Simmons and Snyder in 1958 [2], showed a separation of C_5–C_8 hydrocarbons using a combination of packed columns. According to the authors, their paper clearly demonstrated that "separations can be obtained with this *(heart-cut two-dimensional)* column arrangement which are not normally possible with previously described arrangements of single columns and multiple columns connected in series." In fact, this statement summarizes the power of two-dimensional GC and is still valid today.

At the end of the 1950s, the first hyphenation of (packed column) GC to mass spectrometry (MS) was described. Gohlke showed the separation of volatile organic compounds using on-line time-of-flight mass spectrometry and stated that "single chromatographic peaks containing two or three components can usually be successfully resolved by careful examination of several mass spectra obtained at

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various times during the development of the chromatographic peak" [3]. Less than a decade later, Schenck and Hall demonstrated the potential of hyphenating two-dimensional GC with mass spectrometry, whereby de facto three separation dimensions were available [4].

The introduction of capillary GC (CGC) at the end of the 1950s boosted the resolving power of one-dimensional GC (1D-GC) separations using long capillary columns [5]. Since then, many of the early applications of two-dimensional GC using packed columns were performed on a single capillary column, as illustrated by detailed hydrocarbon analysis in petrochemistry. However, the power of two-dimensional capillary GC configurations was recognized, and applications were published shortly after CGC was finding its way into industrial laboratories [6]. Since the introduction of CGC, many applications have been described whereby capillary columns (and packed columns) are combined in series and selected fractions are transferred from the first column to the second. This technique is called heart-cut two-dimensional GC, and annotated as GC-GC or 2D-GC.

In the historical papers cited above, in-line valves were used to direct the flow from the first column to the second column. Although great progress has been made in valve technology since then, a major breakthrough in the applicability of two-dimensional capillary GC was achieved by the introduction of column switching based on pressure balancing at the column junction by D.R. Deans [7–9]. While in-line multiport switching valves are still used for gas and light petrochemical fractions, the "Deans-switch" principle is currently the most used approach for two-dimensional capillary GC in a wide range of applications, for volatile to low-volatile and non-polar to polar solutes.

During the 1980s and 1990s, commercial 2D-CGC equipment became available, including for instance, the Siemens Sichromat 2 [10], the Chrompack MUSIC system (Multidimensional Switching Intelligent Controller) [11], and the Gerstel MCS [12]. Besides such systems, numerous "home-made" approaches were used. Although these systems were successfully applied, mainly in R&D laboratories working in petrochemical, flavor & fragrance and tobacco industries, the setup of a new application on a new column combination was often found to be quite difficult and required delicate optimization and pressure balancing. Consequently, GC-GC seemed to remain a too complicated "toy," exclusively reserved for high-end users.

In 1991, Liu and Phillips introduced a first configuration allowing to perform two-dimensional capillary GC whereby the entire sample was subjected to two separations. This approach was called comprehensive 2D-GC, shortly annotated as GC×GC [13]. Using a short column in the second dimension and a "modulator" device to heart-cut consecutive fractions from the first dimension separation, a GC separation was realized similar to the concept of two-dimensional planar chromatography, already described in 1944 [14].

Since the introduction of comprehensive 2D-GC, also the interest in heart-cut two-dimensional gas chromatography has increased. Not only comprehensive 2D-GC, but also classical heart-cut 2D-GC has (re)gained lots of interest and currently both techniques are finding their ways to routine laboratories. Obviously, developments in electronic pressure and flow control in state-of-the-art gas chromatographs, new column coupling techniques, fast MS detectors, etc., have catalyzed this evolution.

Nowadays, both GC-GC and GC×GC can be considered as valuable techniques for high-end applications dealing with challenging samples. Both techniques use two (or more) capillary GC columns coupled in series via a "transfer device." In classical two-dimensional GC, the second dimension (^{2}D) column has similar dimensions (length, ID, peak capacity) as the first dimension (^{1}D) column, but differs in stationary phase (or phase ratio). This is different from GC×GC, whereby the entire sample is transferred to the second dimension in very small fractions, typically using transfer windows smaller than the ^{1}D peak width. The second dimension column is very short and has a limited peak capacity, because the second dimension separation needs to be completed in the time frame of the transfer window (modulation time). Comprehensive 2D-GC is further discussed in Chapter 2.2.

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In this chapter, we will discuss the basic principles, experimental setup, and applications of classical heart-cut GC-GC. Rather than attempting a complete historical overview of all possible configurations and applications, we will mainly discuss the state-of-the-art configurations and show examples obtained in the author's laboratory, using GC-GC with mass spectrometric detection.

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Sources of Environmental Pollution: Persistent Organic Pollutants

I. Arslan-Alaton, T. Olmez-Hanci, in New and Future Developments in Catalysis, 2013

Abbreviations

2D-GC	Two-Dimensional GC
AED	Atomic Emission Detector
AFFFs	Aqueous Film Fire-Fighting Foams
ASE	Accelerated Solvent Extraction
ATSDR	Agency For Toxic Substances and Disease Registry
b.w.	Body Weight
BFRs	Brominated Flame Retardants
CAS	Chemical Abstracts Service
CB-209	Decachlorobiphenyl
COP4	Conference of the Parties
DBDE	Decabromodiphenylether
DDD	1,1-Dichloro-2,2-Bis(4-Chlorophenyl)-Ethane
DDE	1,1-Dichloro-2,2-Bis(4-Chlorophenyl)-Ethylene
DDT	1,1-Trichloro-2,2-Bis(4-Chlorophenyl)-Ethane
DLLME	Dispersive Liquid-Liquid Microextraction
dl-PCBs	Dioxin-Like Pcbs
DLPME	Dispersive Liquid-Phase Microextraction
DSPE	Dispersive Solid-Phase Extraction
ECD	Electron Capture Detector
ECEH	European Center for Environment and Health
ECHA	European Chemicals Agency
ECNI	Electron Capture Negative İonization
EFSA	European Food Safety Authority
ELCD	Electrolytic Conductivity Detector
EtFOSAA	Ethylperfluorooctane Sulfonamidoacetic Acid

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FOSA	Perfluorooctane Sulfonamide
GC	Gas Chromatography
GC-HRMS	GC Coupled With High-Resolution Mass Spectrometry
HBCD	Hexabromocyclododecane
HCH	Hexachlorocyclohexane
HRGC-HRMS	High-Resolution Gas Chromatography High-Resolution Mass Spectrometry
HRTOF-MS	High-Resolution Time-of-Flight Mass Spectrometer
HS-CT-LPME	Microwave-assisted Headspace Controlled-Temperature Liquid-Phase Microextraction
IARC	International Agency for Cancer and Research
ITMS	Ion Trap Tandem Mass Spectrometry
K_{ow}	Octanol-Water Partition Coefficients
LC	Liquid Chromatography
LLE	Liquid-Liquid Extraction
LOD	Limit of Detection
LOQ	Limit of Quantification
LRMS	Low-Resolution Mass Spectrometer
MAE	Microwave-Assisted Extraction
MAME	Microwave-Assisted Micellar Extraction
MMSPE	Microporous Membrane Solid-Phase Extraction
MS	Mass Spectrometry
MSPD	Matrix Solid-Phase Dispersion
NHANES	National Health And Nutrition Examination Survey
NIST	National Institute of Standards And Technology
OC	Organochlorine
OCPs	Organochlorine Pesticides
OECD	The Organization for Economic Cooperation and Development
PAH	Polyaromatic Hydrocarbons
PBB	Polybrominated Biphenyl
PBDEs	Polybrominated Diphenyl Ethers
PBT	Persistent, Bioaccumulative, and Toxic
PCDD/Fs	Polychlorinated Dibenzodioxins/Furans
PFBS	Perfluorobutane Sulfonate
PFCAs	Perfluorocarboxylates
PFCs	Perfluorinated Compounds
PFDA	Perfluorodecanoic Acid
PFHxA	Perfluorohexanoic Acid
PFHxS	Perfluorohexane Sulfonate

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PFNA	Perfluorononanoic Acid
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctane Sulfonate
PFOSA	Perfluorooctane Sulfonamide
PFOSF	Perfluorooctane Sulfonyl Fluoride
PFOSi	Perfluorooctane Sulfinate
PFSAs	Perfluorosulfonates
PFTA	Perfluorotetradecanoic Acid
PFUnDA	Perfluoroundecanoic Acid
PGC	Porous Graphitic Carbon
PHWE	Pressurized Hot Water Extraction
PIC FAO	Convention on Prior Informed Consent
PLE	Pressurized Liquid Extraction
PMN's	Premanufacture Notification
PMTI	Provisional Tolerable Monthly Intake
POPs	Persistent Organic Pollutants
PP	Priority Pollutants
SD-DLLME	Solvent-based De-emulsification Dispersive Liquid-Liquid Microextraction
SE	Soxhlet Extraction
SEC	Size Exclusion Chromatography
SFE	Supercritical Fluid Extraction
SPE	Solid-Phase Extraction
SPLE	Selective Pressured Liquid Extraction
SPME	Solid-Phase Microextraction
SWE	Subcritical Water Extraction
TBBPA	Tetrabromobisphenol-A
TCDD	2,3,7,8-Tetrachlorodibenzo-*P*-Dioxin
TDI	Tolarable Daily Intake
TEF	Toxic Equivalency Factor
TEQ	Toxic Equivalence
TOC	Total Organic Carbon
TSCA	Toxic Substances Control Act
UAE	Ultrasonic-assisted Extraction
UNECE	United Nations Economic Commission for Europe
UNEP	United Nations Environment Program
US EPA	United States Environmental Protection Agency
USAEME	Ultrasound-Assisted Emulsification-Micro-Extraction
UWWTP	Urban Wastewater Treatment Plant

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VALLME	Vortex-Assisted Liquid-Liquid Microextraction
vPvB	Very Persistent and Very Bioaccumulative
WHO	World Health Organization
WWTP	Wastewater Treatment Plant

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