



Comprehensive 2D Chromatography

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In general, comprehensive two-dimensional (2D) chromatography (C×C) methods enable the separation of the entire injected sample (first introduction system) on two columns (first and second dimension — ¹D and ²D), characterized by different stationary phases. A transfer device, named modulator (second introduction system), enables the sequential and continuous injection of ¹D eluate fractions onto the ²D column. Separations of each fraction on the ²D column are usually rapid — ideally, each fraction must be analysed before the next one exits the modulator — and are characterized by a fixed time frame (modulation period). Normally, a single detection system is used, to monitor the analytes leaving the ²D column. Hence, a native C×C chromatogram is formed of a sequence of rapid ²D separations, which develop gradually along an x axis. Dedicated software tools are used to transform such one-dimensional data in a planar (2D) format. The ¹D and ²D separations are positioned along an x and y axis, respectively, while peaks are represented with circular/oval shapes. Peak area and colour intensity relate to analyte quantity.

The common benefits of C×C are an enhanced separation space and selectivity, along with the formation of organized elution patterns whenever homologous series of compounds are involved (e.g. triacylglycerols, carotenoids, monounsaturated fatty acids, pyrazines, etc.). A further benefit, related

more specifically to thermal modulation comprehensive two-dimensional gas chromatography (GC×GC), is an enhancement of analyte signal-to-noise ratios. If mass spectrometry (MS) is used as “detector”, then an extremely powerful instrument is formed, composed of three analytical dimensions. The C×C-MS field has seen a great deal of instrumental and software development (involving both industrial and academic entities) over the past two decades, along with the publication of a plethora of application types (food, biological and microbiological, petrochemical, environmental, flavour and fragrance, pharmaceutical, etc.).

The most commonly-used C×C approach has been GC×GC, followed rather distantly by comprehensive two-dimensional liquid chromatography (LC×LC). Other technologies, such as that involving the liquid–gas chromatography combination (LC×GC), have been reported only in a handful of investigations. The first descriptions of GC×GC and LC×LC appeared in 1991 and 1990 [1, 2], respectively, while the benefits of using two consecutive orthogonal separation processes (in planar chromatography) dates far back [3]. However, though the advantages of using GC×GC and LC×LC have been fully demonstrated in a multitude of cases, both techniques are far from established and are still perceived to be used mainly by an elite class of chromatographers. Other reasons exist, such as the power of modern-day GC–MS and LC–MS, which can effectively cover many analytical requirements, and financial aspects. We imagine that such a scenario, at this point, will remain so for a long time. It is noteworthy that the use of GC×GC or LC×LC is well within the reach of anybody with a decent knowledge of chromatography basics and adequate training.

The present ABC “Comprehensive 2D Chromatography” Topical Collection confirms the current trends in the field. In fact, among in well over twenty papers, three are based on LC×LC and the remaining ones on GC×GC. With regard to the LC×LC contributions, two are focused on the determination of food nutraceuticals (in one case, focus was also devoted to the use of “greener solvents”) and the other on dilution effects. Among the GC×GC manuscripts, there is one review paper (related to the plastic recycling process),

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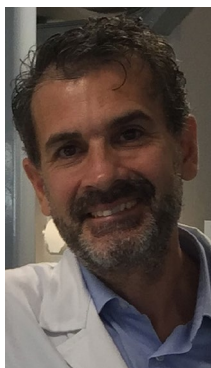
while the remaining are research papers, describing diverse untargeted and targeted applications (plastics, foods, microorganisms, sediments, fuel, saliva, pharmaceuticals), data processing tools, theoretical/practical issues, and instrumental evolution (^2D temperature-programming). Food analysis is herein the main GC \times GC applicational field reported.

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Peter Q. Tranchida acquired his PhD in “Food Chemistry and Safety” in 2006, currently occupies a position as Associate Professor in Food Chemistry at the University of Messina (Italy), and is Coordinator of the Master's Degree Course in Food Science and Human Nutrition. His research activities are focused mainly on the study of food samples (not only) by using advanced chromatography processes, prior to mass spectrometry (MS) detection. In particular, a great deal of his research has been directed towards the development and application of classical multidimensional and comprehensive two-dimensional chromatography systems. Specifically, in the

fields of classical multidimensional gas chromatography, multidimensional liquid-gas chromatography, and comprehensive 2D gas

chromatography (GC \times GC). In terms of MS systems, he currently uses rapid-scanning single quadrupole, triple quadrupole, and low- and high-resolution time-of-flight devices. In the field of GC \times GC, he has performed applications, method optimization studies, and instrumental development and introduced novel approaches to flow modulation. In 2012, at the “9th GC \times GC symposium”, held in Riva del Garda, he was awarded the “John Phillips Award”, for his outstanding achievements in the field of comprehensive two-dimensional gas chromatography. In 2019, at the “16th GC \times GC symposium”, held in Fort Worth (Texas), he was awarded the “GC \times GC Lifetime Achievement Award”. He is currently Associate Editor of *Journal of Separation Science* (Wiley).



Luigi Mondello is Professor of Analytical Chemistry at the University of Messina, Italy. He is the author of about 700 publications (research articles, book chapters, and reviews) and 1500 conference presentations (of which 220 invited/plenary lectures). His research interests include high-resolution chromatography techniques (HRGC, HPLC, HRGC-MS, HPLC-MS, OPLC) and the development of hyphenated (LC-GC-MS, GC-GC) and multidimensional “comprehensive” (GC \times GC,

LC \times LC) techniques and their applications to the study of natural complex matrices. He is President of the Steering Committee of the Italian Separation Science Group of the Italian Chemical Society, Editor in Chief of the *Journal of Essential Oil Research* (Taylor & Francis), and Editor of *Analytical and Bioanalytical Chemistry* (Springer). In February 2006, he was awarded the “HTC-Award” for the most outstanding and innovative work in the field of hyphenated chromatographic techniques. In May 2008, he was awarded with the “Silver Jubilee Medal”. In October 2008, he received the COLACRO Medal. In September 2012 he was awarded with the “Liberti Medal”. He has been awarded in “The Analytical Scientist Innovation Awards” (TASIA 2013 and 2015, 2016). In September 2014, he was the recipient of the IFEAT Medal. In September 2017, he was the recipient of the “Robert Kellner Lecture Award”. In May 2019, he received the 2019 Herbert J. Dutton Award from the Analytical Division of the AOCS. In September 2020, the Presidium of the Committee of the Analytical Chemistry of the Polish Academy of Science and Polish Chemical Society assigned him the Prof. A. Waksmundzki Medal Award. In December 2021, “The Chromatographic Society” awarded him with the “A.J.P. Martin Medal 2022” for his “outstanding contributions to the advancement of separation science”. He is present in the list of the “Top Italian Scientist” (via-Academy). The *Analytical Scientist Journal* has included his name in the “Power List” among the top 100 most influential people in analytical sciences (2013 and 2015) and in November 2017 in one of the top ten worldwide scientists in the field of Separation Science.