Chapter

Introductory Chapter: Gas Chromatography - The Most Versatile Analytical Technique

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1. Definition and short history of gas chromatography

Gas chromatography (GC) is a type of chromatography. According to the International Union of Pure and Applied Chemistry (IUPAC) recommendation, gas chromatography is defined as a separation technique in which the mobile phase is a gas. Gas chromatography is always carried out in a column [1]. GC is a separation and detection method for sample mixtures, whose components can be volatilized without thermal decomposition. The analytical procedure is used for the determination of organic substances; usually molecules have a molecular mass of less than 500 g/mol and a boiling point of less than 400°C. GC is a technique used to separate mixtures of gaseous chemical compounds based on differences in the compounds' relative affinities for a solid (gas-solid chromatography) or liquid (gas-liquid chromatography) stationary phase held within a column.

Gas-liquid partition chromatography was invented by Martin and James from the National Institute for Medical Research, London, in 1952. The invention of this technique is generally attributed to the inventors in their 1952 published paper in the *Biochemical Journal* [2]. In this publication the theory of the partition column has been extended to cover a compressible mobile phase, and gas-liquid partition columns were described for the separation of volatile fatty acids. In the same year, the *Nobel Prize* in chemistry was awarded jointly to Martin and Synge for their *invention of partition chromatography*. Starting from this time, gas chromatography has become one of the most important and widely applied analytical techniques in modern chemistry. The first commercial gas chromatograph was introduced in 1955 by Perkin-Elmer (USA). Subsequently, this method was used to study petrochemical products. Today, gas chromatography is one of the most widespread investigation methods of instrumental analysis. This technique is used in the laboratories of the chemical, petrochemical, and pharmaceutical industries, in the research institutes and also in the clinical and environmental and food and beverage analyses. Recent developments in GC have resulted in the introduction of better and selective fused silica capillary columns and methods for sample preparation. Newer separation and detection solutions, such as fast GC, multidimensional separation GC techniques (GC × GC), and hyphenation of GC and GC × GC with mass spectrometry (MS), with triple quadrupole mass spectrometry and with time-of-flight mass spectrometry (TOF-MS), have been developed and become industrial routine. Analytical pyrolysis (Py) technique hyphenated to GC and GC/MS has extended the range of possible tools for the characterization of synthetic polymers and copolymers. This technique has been

used extensively over the last 30 years as a complementary analytical tool used to characterize the structure of synthetic organic polymers and copolymers, polymer blends, biopolymers, and natural resins [3].

2. Multidimensional gas chromatography

Developed by Phillips and coworker at the Southern Illinois University (USA) in the early 1990s, comprehensive multidimensional GC (GC × GC or 2D GC) is a powerful technique for samples containing very large numbers of compounds of interest and also for samples which exhibit high chemical complexity. This technique can be used to separate very complex mixtures, such as those found in the petrochemical, environmental, and food and fragrance industries [4–6]. The method uses two capillary columns, typically of very different polarities, installed in series with a modulator in between. The first column is in principle nonpolar or low polar, and the second column is polar. The length of the first column might typically be 20–30 m, the inner diameter 0.25 mm, and the film thickness 0.25 μm. The second column is typically shorter (1–2 m), the inner diameter is narrower (0.1 mm), and the stationary phase is thinner (0.1 μm), to allow for faster separations. The entire assembly is located inside the GC oven [6]. The modulator collects effluent from the first column for a fraction of the time equal to peak width. The modulator focuses the material collected from each cut into a very narrow band through flow compression. It introduces the bands sequentially onto the second column, resulting in additional separation for each band injected onto the second column [4–9]. The most common data transformation is the construction of a 2D representation, in which one axis represents the separation on the first column (first dimension), and the other axis represents the secondary column separation (second dimension). Therefore, the look of GC × GC chromatograms appears completely different from conventional GC chromatogram showing a two-dimensional plane where analyte spots are scattered about [7, 8]. A contour plot, using elevation lines or color coding, represents the signal intensity. 2D GC data are primarily used for

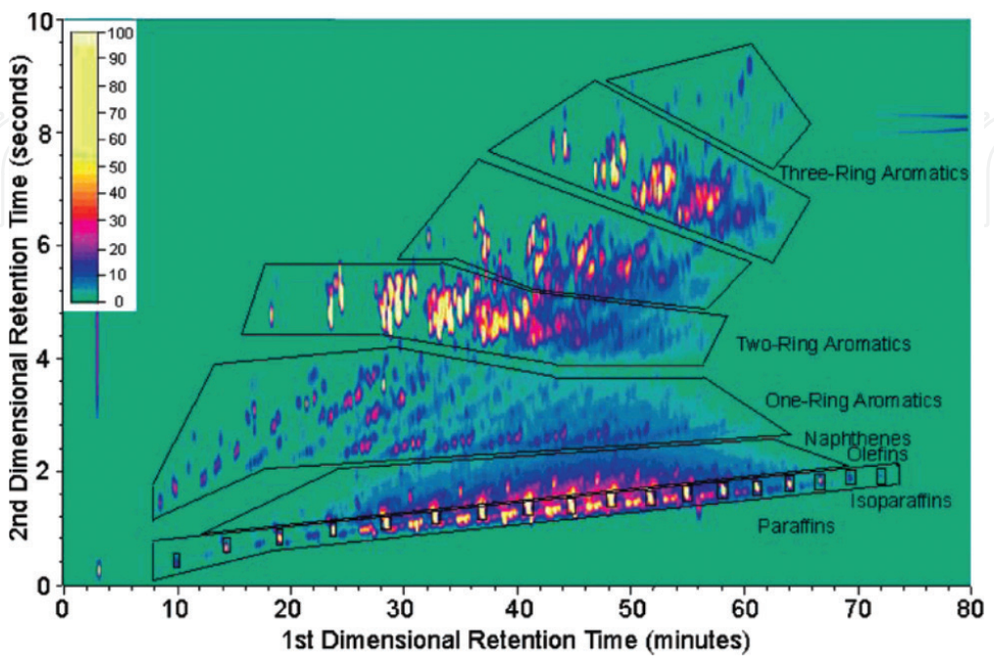

Figure 1.
2D GC plot of a refinery stream boiling at diesel temperature range. The scale indicates the relative signal intensity. Figure reprinted from Ref. [10] with permission from ACS.

qualitative analysis; however, quantitative multidimensional GC analysis is also possible [9]. **Figure 1** shows an exemplary 2D GC plot of a refinery stream boiling at diesel temperature range [10].

In this book, state of the art of gas chromatography and new developments and applications are presented. New sample preparation techniques, derivatization methods, and hyphenation with mass spectrometry are described.

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