Comprehensive Two-dimensional Gas Chromatography

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Gas chromatography (GC) is one of the versatile analytical techniques used in both qualitative and quantitative studies. With the increasing synthesis of chemical compounds, the hazardous materials released to the environment increases at an alarming rate. So the importance of analyzing and separately identifying these contaminants in the environment increases at the same rate. The separation power of Gas chromatography using traditional single column fails when analyzing samples containing more than 150 to 250 compounds [1]

The resolution of a separation depends on several factors as shown in the equation (1),

$$R_s = \frac{k}{k+1} \times \frac{\alpha}{\alpha - 1} \times \frac{\sqrt{N}}{4} \qquad (1)$$

Where N is the number of plates, α is the separation factor of a pair of solutes, and k is the retention factor of the most retained solute. If we think of the column properties, increasing the number of plates (N) should improve the resolution of the separation. But the number of plates depends on the plate height and column length. To increase N, plate height should be minimum while having a long column length. Most straightforward option is to increase the column length as several factors such as mobile phase and stationary phase properties affect the plate height. But this results in a much higher analysis time. A better example is once a 450 m column was used by T. A. Berger [2] to separate constituents in Gasoline. He was able to separate 970 constituents but the analysis time was 11 hours. So the best possible way to improve the resolution is to increase the separation factor α.

The recent studies have expanded the capabilities of GC to a much higher level. Among them Multidimensional Gas Chromatography (MDGC) provides promising capabilities which increases the separation factor. Multi-dimensional analysis in chromatography can be considered as any technique that connects two or more different separation steps of which at least one of the steps involves a chromatographic separation. So that Liquid chromatography (LC)-GC, GC-GC and GC-spectroscopic detection like GC-mass spectroscopy (MS) are typical multi-dimensional methods.[3]

Simply this is achieved by connecting multiple (mostly 2) columns with different phase sensitivities by a modulation device.[4]. This approach consists of two distinct methods. "Heart-cut" approach (GC-GC), where only a fraction of the sample from the first column is guided to the next column and the Comprehensive 2D GC (GC-GC) all the compounds eluting from the first column are subjected to a second dimension of separation. This technique is called comprehensive two dimensional (2D) gas chromatography (GC×GC).

The Heart cut approach (GC-GC) is helpful in separating compounds with similar retention times. This is done by connecting two classical columns. So the compounds with similar retention time in the first column would resolve in a second column with different separation properties.

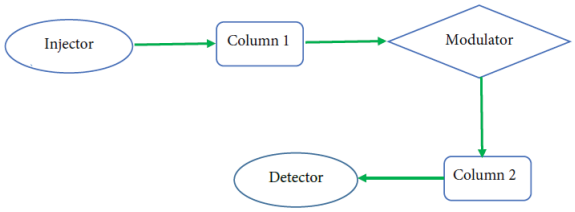
In the second method, the comprehensive 2D GC (GC×GC), improves the peak resolution and the peak capacity related to the separation. For an effective separation using GC×GC, a set of rules are being followed as presented by J. C. Giddings [5].

1. Sample analytes must undergo 2 different separation mechanisms
2. The separation resulted by a one column must be retained by the other (Avoid mixing)
3. The second column/ dimension must be significantly faster than the first one

Although it is difficult to have completely different separation mechanisms [4], columns with different polarities are used. A combination of polar and Non-polar are generally being used. To ensure a faster second column, usually a shorter column is being used, which fulfills the 2 and 3 criteria. If the column 1 is non-polar and the second column is polar, the arrangement is known as "conventional" as it was the earliest practice. If a polar column placed as first column, known as inverse

set.[6]

As the main emphasis of this article is on Comprehensive 2D GC, understanding the main components is important. The following diagram shows the basic parts of the setup.



Basic parts of a comprehensive 2D GC system

The setup differs from the conventional GC system with the "modulator" mechanism which connects two columns. The modulator is responsible for rapid sampling of eluent from column 1 and "comprehensively" directing it to the second column. It actually acts as the injector for the second column. The sampling rate is known as Modulation period and can be adjusted from 1^{-10} s. This is adjusted in a way to ensure the separation from column 1 is retained at the end of the whole process. The injection pulses are narrow and result in faster secondary separations.[4] There are mainly two types of modulators as Thermal and Flow modulators based on their mechanism. The thermal modulators use cryogenic conditions to trap and focus the analytes coming from column 1 and then heat up rapidly to direct them into the second column. The flow modulators on the other hand are simple and low costly to maintain [6].

For the detector data-acquisition rate of 50–200 Hz will be necessary. This allows flame-ionisation detection (FID) and electron-capture detection (ECD) and time-of-flight mass spectrometry (TOF-MS) to be used as detectors.[3]

If the two columns were directly connected to each other, the resulting data from the detector will be just data for a mixed phase separation which is one dimensional. But the modulator provides a reference time signal for sampling the first column and injecting the second column. So that the continuous signal obtained from the single detector at the end of the second column can be resolved into a 2D signal. [5]

The process related to operation and data obtaining can be summarized as Modulation, Transformation and visualization. The results come from continuous analysis of column 2 eluents, a large number of short chromatographs (resolved co-eluted peaks from the first column). These short chromatographs are summed up to obtain a raw chromatograph also with the experimental modulation data. Then the data converted to a 2D plot, retention time in the first column vs. Retention time in the second column using software programs. For the visualization, 3D plots are prepared. This GCxGC chromatogram (contour plot) is similar to a topographic map where the first dimension/column retention time is on the x-axis, the second dimension/column retention time on the y-axis, and peak intensities are on the z-axis [6].

Considering some of the applications of this 2D GC, all of them make use of the high resolution power of this method. The Petrochemical and geochemical analysis has many advantages from this method to resolve compounds from natural samples with closer retention times. Also the fact that it can be operated with a FID detector instead of a Mass Spectroscopic detector while giving highly resolved results has raised the interest in the industry. Similarly, in the natural product sector this method can be used to resolve compounds which were difficult to study with conventional 1D GC. As mentioned at the beginning, this method is also helpful in environmental analysis, where hundreds of compounds can be identified at a single run.[3] GCxGC fingerprinting has been used successfully in the analysis of petroleum hydrocarbons, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and volatile organic compounds (VOCs).

Although this is a recently introduced adaptation of gas chromatography, endless application in a variety of fields will make it a common lab technique in the near future.

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The National Research Council Investigator Driven Grants 2020, Grant Number 20-086, by Dr. J. A. T. C. Ariyasena, Prof. C.F. Poole, and K.P. Hewage is acknowledged.

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