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Two-dimensional gas chromatography – principles and application in fruits analysis

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ABSTRACT

Two-dimensional gas chromatography is a rapidly developing analytical technique. One of the major uses of this technique is its use for food analysis. The paper presents the principle of operation and history of this analytical technique. The specification of the two-dimensional gas chromatography technique has been discussed. The principles of separation of ingredients and application of the method, particularly in the analysis of food products, have also been described. A literature review was also done, presenting the use of two-dimensional gas chromatography for the analysis of fruit and fruit products.

***Keywords*:** two-dimensional gas chromatography, history, principles, applications, aparature

1. INTRODUCTION

Fruits are important element of human's diet. We should eat several servings of fruit a day. Fruits belong to foods that quickly spoil and lose their health and taste. It is extremely important to control their quality. One of the quality control measures is the analysis of the volatiles. The composition of the fruit matrix is variable and often complex. Researchers look for new solutions, thanks to which accurate analysis is possible. One technique for analyzing volatile fractions is two-dimensional gas chromatography (GC×GC). It is an analytical technique used to separate volatile organic compounds. In this technique, two independently

linked chromatographic columns are used. The polarity of the fill is one of the properties of the columns, distinguishing them from one another. This improves the separation possibilities compared to standard gas chromatography. Another important distinguishing element of both analytical techniques is the GC x GC modulator. It is a connection between two columns.

The birth of two-dimensional gas chromatography is assumed to be the ninetieth year of the last century [1]. In recent decades it has become increasingly common and more and more used analytical technique. It allows analysis of samples with very complex matrix composition.

2. COMPREHENSIE TWO DIMENSIONAL GAS CHROMATOGRAPHY

2. 1. History

J. Calvin Giddings was the creator of the idea of separating the components of the mixture using the GC×GC technique, proposed in 1984 [2,3]. The professor assumed that the best results of GC×GC analysis would be obtained when the separation mechanisms in both dimensions are completely different from each other and strictly orthogonal. The complete GC×GC technique was intended to solve the problem of limited peak capacity and the difficulty of separating certain compounds in the classical GC. It was essential to find a suitable way to divide the components of the mixture into the first column by dividing the whole separation process into the second column by using another separation mechanism while still separating the components obtained in the first column. In the 1990s, J. Phillips proposed the implementation of the GC×GC modulator. Officially recognized as the year 1991, the GC×GC is equipped with a modulator as the year of the launch of the complete two-dimensional gas chromatography technique [4]. Further development of GC×GC consisted mainly in the construction of new types of modulators, as well as appropriate software that would enable the automation of the processing of large amounts of data [1].

2. 2. Priniples of separation

The principle of separation of two-dimensional gas chromatography is based on the interaction of analytes with the stationary phase and the mobile phase. As a mobile phase, inert gas, unreacted with analytes, mostly helium or nitrogen, is used. Introduced into the chromatography system, the sample is evaporated in the injector and entrained through the carrier gas stream. Separation of chemicals is possible through the use of two serially-bound, stationary polarization columns with different polarity. The heart of the system is a modulator, which combines both chromatographic columns and the transfer of individual components from one column to another [5]. Eluat, together with analytes, every few seconds is washed with the carrier gas stream from the first column, and each chromatographic peak obtained is divided into fragments. Each fragment is passed to the second chromatographic column. During modulation, the mass of the analyte does not change, therefore the height of the peak is increased, offsetting the decrease in its width, which contributes to increasing the sensitivity of analysis [1]. At the end of the system there is a detector, which reacts to the presence of the dissolved chemical producing a signal that is sent to the registrar system.

2. 3. Aparature

The scheme of used aparature is shown in the Figure 1.

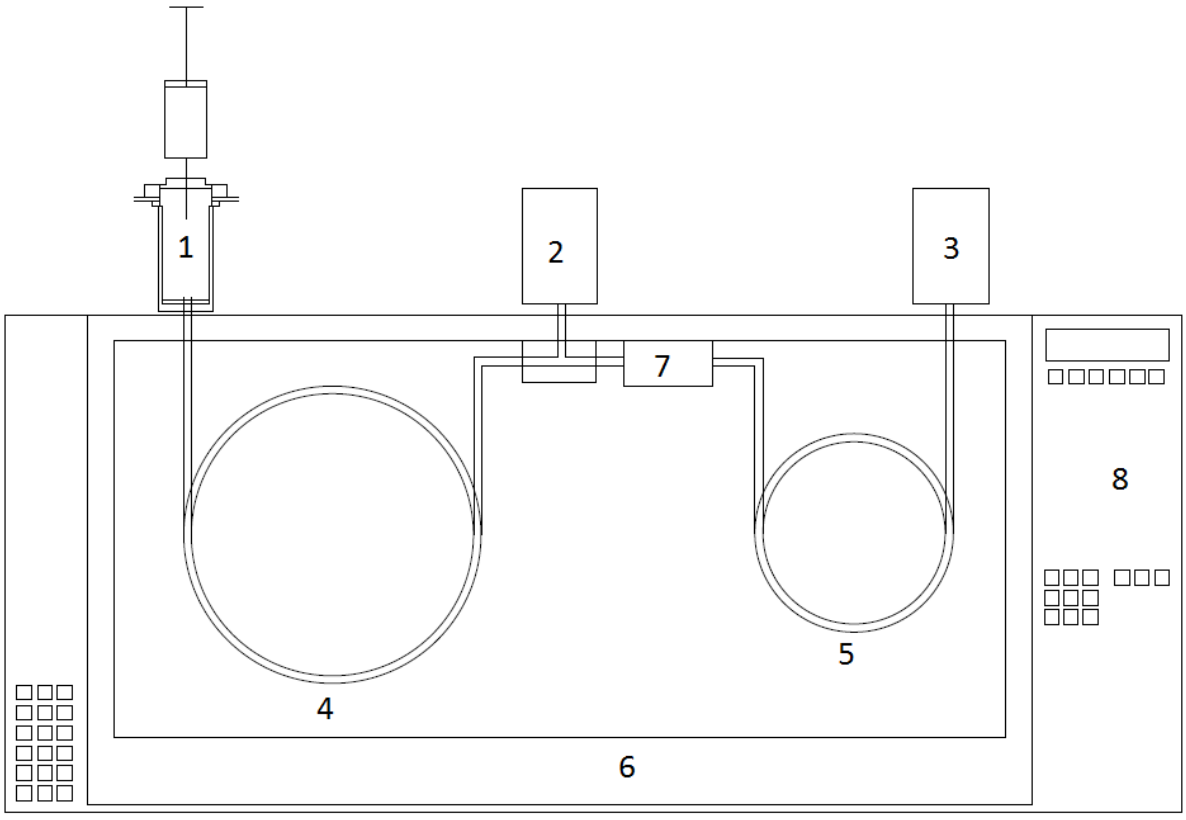

Figure 1. Scheme of two-dimensional gas chromatograph

1. Injector - It is a component of the chromatographic system used to entry the sample into the chromatographic column. In the two-dimensional gas chromatography the same dispenser types are used, as in GC.

2, 3. Detector - A device for detecting components. The most commonly used is flame ionisation detector - FID. Sometimes an electron capture electron microscope is also used

M-ECD, as well as atomic emission detector AED and SCD sulfur chemiluminescence detector. The best solution, however, is the aforementioned FID, due to its good dynamic properties.

4. Chromatogrphy column 1 - The first dimension chromatography column is typically 15 to 30 m in length and has an internal diameter of 0.25 mm. Contains a stationary film with a thickness of 0.25 to 1.0 µm. In this case 100% polydimethylsiloxane or 95/5% phenyl / methyl siloxane is the non-polar stationary phase. The chromatographic column allows generation of peaks of approximately 10-20 s width.

5. Chromatographic column 2 - A second dimension chromatographic column filled with another stationary phase than the first column. Its length is usually from 0.5 to 1.5 m and the inside diameter is 0.1 mm. Due to its higher efficiency compared to the first column, the stationary film layer is also thinner and ranges from 0.1 to 0.25 mm. The most commonly used stationary phases are 50/50% phenyl / methyl siloxane or Carbowax. Chemical compounds must leave this chromatographic column in a very short time, shorter than the modulation period.

6. Chromatographic oven - A gas chromatograph element responsible for maintaining the chromatographic system at a suitable temperature to ensure effective separation of the analyzed components of the mixture.

7. Modulator - The element of the chromatographic system responsible for transferring the eluent from the sample from the first chromatographic column to the other [6]. It can have different configurations, such as rotary slit heater, longitudinally modeled cryogenic system, thermal nozzles, loop modulator. Irrespective of the type of modulator, the modulator function is:
• Continuous accumulation of small amounts of the analyte from the first column,
• Adjusting their retention time and dispensing frequency
• Introducing fractions into the second dimension column [7].

8. Recorder - This is a device in which the signals received from the detector are recorded. The most common is a PC with a built-in transducer card.

2. 4. Comparison of GC×GC with traditional 1D-GC

The GC×GC technique has several advantages over the classic one-dimensional GC, for example:

- greater distribution capacity and higher peak capacity [8],
- allows analysis of samples with complex matrix composition [9],
- allows identification of trace or ultra-trace analyte [10],
- allows for more detailed quantitative and qualitative analysis.

2. 5. Application of GC×GC in fruit analysis

Two-dimensional gas chromatography is a technique often used in many different areas of chemistry. It was originally used to analyze petroleum samples. Over time, it was discovered. that it allowed for analysis for other complex matrices. Increasingly, the GC×GC technique is used for forensic, environmental, clinical and food analysis [11]. In the table below some applications of GC×GC in fruits analysis are showed (Table 1).

Table 1. Application of GC×GC in fruit analysis

Fruit or fruit product	Analytes	Detector type	Modulator type	Year	Ref.
apples, pears, quincefruits	volatile compounds	qMS	cryogenic	2010	[12]
apples, peaches	pesticides	TOF-MS	cryogenic	2003	[13]
pasteurised orange juice	odour active compounds	TOF-MS	cryogenic	2015	[14]
grapes	monoterpeneoids	TOF-MS	cryogenic	2007	[15]
bananas	aroma-actibe volatiles	FID, MS	cryogenic	2015	[16]
apples	metabolites	TOF-MS	cryogenic	2012	[17]
apples	volatile compounds	TOF-MS	cryogenic	2013	[18]
terebinth fruits	volatile compounds	TOF-MS	cryogenic	2014	[19]
blueberries, cranberries and cape gooseberries	terpenes	TOF-MS	cryogenic	2016	[20]
cranberries and cape gooseberries	terpenes	TOF-MS	cryogenic	2015	[21]
blue honeysuckle berries	terpenes	TOF-MS	cryogenic	2014	[22]
grapes	pesticides and organic pollutants	TOF-MS	cryogenic	2010	[23]
grapes	pesticides	TOF-MS	dual stage thermal modulator	2008	[24]
strawberries	volatile compounds	TOF-MS	cryogenic	2013	[25]
apple juice	pesticides	MS	-	2009	[26]
grape	pesticides	FID/microECD	air modulator	2009	[27]
red grapefruit extract	pesticides	qMS	the loop modulator	2007	[28]
strawberries	volatile compounds		cryogenic	2005	[29]

3. CONCLUSIONS

Gas chromatography is an effective solution in the analysis of fruit and fruit products. In contrast, the use of two-dimensional gas chromatography allows for more sensitive analysis and provides more detailed quantitative and qualitative analysis. Despite this, the high price of the apparatus and the problems involved in carrying out the quantitative analysis makes it impossible to put it into most industrial laboratories [30].

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