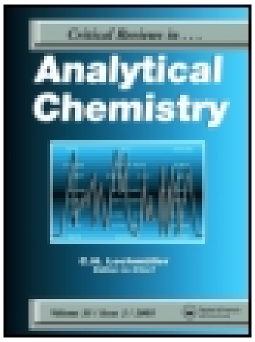

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Two-dimensional gas chromatography coupled with mass spectrometry in food analysis

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ABSTRACT

The development of instrumental analytical techniques provided the opportunity for in-depth characterization of many food matrices. In particular, the use of gas chromatography coupled with mass spectrometry gives impressive results in terms of quality and authenticity testing, conducting food freshness evaluations and contamination assessments. A new variant of gas chromatography, namely two-dimensional gas chromatography, and various versions of mass spectrometry have been developed since last 15 years and they still remain at the time of their renaissance. The present critical review is focused on the use of two-dimensional gas chromatography coupled with mass spectrometry for qualitative and quantitative reasons in food analysis. It is explained how powerful analytical tool is above-mentioned technical solution. Special attention is devoted to the issues related to the development of this technique during last years in terms of key construction elements, such as modulators and MS detectors. Finally, the critical discussion on many various aspects including advantages and more

important disadvantages, caused probable moderate interest of this solution, in food analytics is concerned.

KEYWORDS: two-dimensional gas chromatography, mass spectrometry, food analysis

1. Introduction

Despite of the development of many instrumental analytical techniques, the sensory analysis is still the most often used technique in food analysis. This classical approach is characterized by many limitations, such as the fallibility of the human factor, low reproducibility and repeatability of the results, as well as the unfeasibility of identifying compounds affecting taste and no possibility of performing a quantitative analysis [1-17]. Therefore, the popularity of hyphenated techniques, especially gas chromatography coupled with mass spectrometry, is growing to a great extend and the identification and quantitation of volatile compounds in foodstuffs becomes possible. Due to the high separation power of chromatographic systems complemented by mass spectrometry detectors, characterized by high sensitivity, it is well known that using these systems enables the identification of chemical compounds on the basis of their fragmentation patterns at least in the range of one part per billion concentration [18-24]. Nevertheless, many foods are considered as a very complex matrices and even more sophisticated equipments were required to expand the state of knowledge in food sciences. Two-dimensional gas chromatography (GC×GC) was first reported in 1991 by Liu and Phillips and it was and revolutionary invention responding to the scientific needs [25]. GC×GC technique constitutes an alternative to the classical one-dimensional chromatography. Separation of sample constituents using is GC×GC systems is based on at least two specific properties, like volatility, polarity or chirality, which increase peak capacity and separation power. For these reasons, compounds characterized by similar properties (e.g. boiling point) are successfully separated in GC×GC system, in contrast to one-dimensional gas chromatography [26]. In the past 25 years, a number of varieties of modulators has been appeared and it ensures a significant development of GC×GC technology. Almost decade later, namely in 2000, the first GC×GC food analysis was presented by Dimandja et al. [27]. He described investigation based on fame ionization detection (FID) and it was the beginning of testing foods using the GC×GC systems. After 2 years, a first use of mass spectrometry combined with GC×GC was done by Shellie and Marriott on food sample [28]. They used a single quadrupole MS (qMS) to monitor second-dimension enantiomer separations in a bergamot essential oil.

The present author of this work has investigated the GC×GC–MS studies from 2001, up until the end of 2017 year, with a total number of 252 food-related papers found. The collected data gives a good view on the utilization of various GC×GC–MS systems in food analysis. Most of the applications can be classified as a qualitative ones, which were carried out by the use of cryogenic modulators and time-of-flight version of MS detectors. So far, less than 20 papers were published, in which the quantitative GC×GC–MS results of food samples were presented. This work constitute a critical summary of state of the art of GC×GC–MS technique used in food analytics. The special attention is devoted to key element of GC×GC systems, namely to modulator technologies, and future trends in detection and quantitation of substances using MS detectors. A total number of 150 applications of GC×GC–MS were shown in food investigations.

2. Two-dimensional gas chromatography

2.1 Comparison of one- and two-dimensional gas chromatography in the context of their use in food analysis

Gas chromatography is one of the most often used instrumental analytical techniques used in food testing. The overarching aim of scientists developing chromatographic techniques is striving after increasing the separation capacity of the chromatographic system. This is related to an increase in the capacity of chromatographic peaks. It is estimated that while using one-dimensional gas chromatography (1D-GC), it is possible to obtain a maximum value of chromatographic peaks amounting to 1800 (while using a capillary chromatographic column with a length of 100 m and the inner diameter of 0.1 mm). Complete, two-dimensional gas chromatography (GC×GC) is a response to the demand of increasing the separation capacity of the chromatographic system. It is intended for research, focusing on samples constituting complex matrices; however, food matrices belong to the most complex ones [29]. Despite the obvious advantage of GC×GC and 1D-GC over the possibility of detecting and determining new substances in food matrices, the number of studies on food analysis using the GC×GC is relatively low as compared to the application of 1D-GC in this scientific field. This may be caused by a significantly higher cost of research instruments and a higher price of a single analysis. Examples of using one- and two-dimensional gas chromatography in food analysis are presented in Table 1.

On the basis of data presented in this table, it can be seen that the number of detected chemical substances calculated per unit of time (1 min.) is much higher than if GC×GC is used than the use of 1D-GC [35,36,44,45,65]. Moreover, the GC×GC technique is used for routine food testing. Its use for this purpose makes it possible to significantly reduce the time of single analysis [13,43] [50,51].

Despite numerous advantages connected with the use of the GC×GC technique, this technique is not as broadly used in food analysis as the 1D-GC technique. This may be caused by a much higher consumption of media and a higher wear of chromatographic columns, in particular, ones filled with the stationary phase. The operating costs are also considerably higher, and the price of the GC×GC-MS set of instruments is one of the highest ones on the market as far as analytical instrumentation is concerned. Moreover, the use of two serially-connected chromatographic columns is connected with many limitations. It is more difficult to select an appropriate set of chromatographic columns dedicated for a given application than to select one chromatographic column in the case of using the 1D-GC technique. The number of analysis required for the optimisation stage for analytical methodology in which the use of GC×GC is taken into account is much higher than for the classical 1D-GC technique. In food testing, the use of a secondary chromatographic column may determine the maximum temperature in the chromatographic temperature programme. This significantly influences the number of detected medium-volatile substances. The use of high-temperature chromatographic separation conditions is always connected with higher degradation of the stationary phase of one of chromatographic columns. A polar stationary phase undergoes degradation most often, e.g. of the DB-Wax/SolGel-Wax type, which is mostly use as the stationary phase of the secondary chromatographic column [7,67,80]. Apart from thermal degradation, it can very often undergo oxygen degradation. For tests of some food matrices using the GC×GC technique, the system of chromatographic columns of the polar×nonpolar stationary phase allows for detecting a broader spectrum of analytes than in the case of the classic system of chromatographic columns of the nonpolar×polar stationary phase [57]. In addition, it is possible to use other combinations of a serial connection of chromatographic columns used in the GC×GC system, e.g. a system of polar×semipolar [34] and nonpolar×semipolar stationary phase chromatographic columns. The latter of the chromatographic systems is characterised by high temperature stability, and its use allows for the introduction of higher operating temperature of the chromatographic oven [38]. To separate a considerable number of racemates and the specification of the enantiometric purity of the separated analyte mixture, systems of chromatographic columns were filled with a chiral stationary phase [81]. Using a set of two serially-connected chromatographic columns, one must also take into account that the inner diameter of these columns may differ (it usually falls within the range from 0.1 mm to 0.25 mm). For this reason, additional compensation of carrier gas is required, which in many cases makes it impossible to apply a few temperature ramps within one chromatographic program [77,78,81].

2.2. Important and new technical solutions in modulator science

In recent years there has been a rapid development of modulator technologies. This entails continuous striving for miniaturization and reduction of both production and performance costs of analytical devices. There is a trend for portable devices, which also concerns gas chromatography. The ability to conduct field measurements greatly increases the application range of chromatographs, also in food analysis, in view of decreasing costs associated with transporting the sample to the laboratory. A few years ago, the development of portable multidimensional gas chromatographs would be impossible, mainly due to modulator requirements. At present, attempts are being made to produce multi-dimensional gas chromatography. Nevertheless, despite of considerable achievements in miniaturization, the development of multi-dimensional gas chromatography is still mainly focused more on enhancing the resolution and much greater performance of the equipment, as exemplified by the GC × GC-HRTOF, which is described in section 3 of this article.

Referring to the basics, the modulator is often called the “heart” of a two-dimensional system of gas chromatography. It is used to concentrate the mixture of analytes eluting from the first chromatographic column in the time specified as the modulation period and transfer them quantitatively to the front of the secondary chromatographic column. The GC×GC system is used for comprehensive food analysis thanks to the use of modulators [84-98], which guarantee that modulation is performed within a broad range of temperatures. It is particularly important in research that is aimed at determining aromatic compounds in food. These compounds belong to volatile chemical compounds, which is why modulation is performed at extremely low temperatures. In turn, if pesticides in foods are determined, the modulator used can be a device operating at high temperatures. An important feature of modulators is their stability during operation and a low refrigerant consumption. It is particularly important for routine tests. In such tests, it is the cost of a single analysis that matters. Consumable-free modulators were also designed in which modulation takes place with no refrigerant. .

According to manner of operation, modulators can be divided into thermal and flow modulators. It should be noted that the highest peak capacity and sensitivity are obtained using classical cryogenic modulators,[106]. In addition, the use of such systems is most appropriate for mass spectrometry hyphenation [104]. One of the latest liquid nitrogen based cryogenic modulators is a single-stage modulator with dedicated liquid nitrogen delivery system [106]. Principle of operation of this device is based on the usage of the relationship between the temperature of carrier gas and its viscosity. It is worth to mention that all cryogenic modulators currently available on the market are only dual-stage modulators. One of the new requirements for cryogenic modulators is to limit the use of coolants to the cold stage. This reduces the use of liquid nitrogen and reduces the size of the device. The most common solution is to use thermoelectric cooling, for example using Peltier cells. An example of such a system may be a temperature-programmed microfabricated modulator, as described by Collin et al. [101,102]. This two-stage modulator is small in size (less than 1 cm^2), and because of the programmable cooling (from -20°C to 0°C) as well as heating (from 100°C to 220 C) significantly increases the possibilities of optimizing the operation of the device. The drawback of thermal modulators is the possibility of temperature crosstalk between the modulator and the GC oven. The solution may be a modulation system that is outside the chromatographic system [103]. This device, called thermal independent modulator, works without coolants and both micathermic heating and thermalelectric cooling are used for modulation. Another solution is the single-stage modulator proposed by Jacobs et al. [104]. In 2017, Mucédola et al. proposed a low-cost heater-based modulator, which can be used both in GC×GC-FID and GC×GC-MS systems [107]. This DIY system is based on the use of a metal capillary loop and has been developed for laboratories that cannot afford commercially available modulation solutions.The advantage of thermal modulators, especially cryogenic ones, is the possibility of performing modulation in a broad range of temperatures, which allows for determination of volatile and medium-volatile chemical compounds occurring in food. The most important is fact that thermal modulators are compatible with mass spectrometers.

Flow modulators, namely valve based devices, due to their simplicity, are increasingly used for routine multidimensional gas chromatography analysis [108-117]. Until recently, the main drawback was an increased gas flow rate due to the mixing of analytes with the carrier gas, making use of such modulators with mass spectrometry very difficult. There are currently commercially available solutions in which such modulators are used in GC × GC-MS. This modulator uses so called Multi-Deans Switching, which limits fluctuations in retention time [115]. The latest type of flow modulator is the multi-mode modulator developed by Seeley et al. [116]. This system can be used in traditional heart-cutting GC×GC, low duty cycle devices and also as a full-transfer modulator. In this type of system, the modulation is done in the joining capillary, and its dimensions and position of the columns in the capillary determine the operation mode of the device. The advantage of this solution is the ability to easily remove and replace the capillary when it is contaminated with a sample's matrix or by a column bleed. One of the latest solutions is the flow modulator (FM) that guarantees a low gas pressure at the modulator output (GC × LP GC) [118]. An active construction design of valve-based modulators is reversed-inject flow modulator [119] and four-stage, low-flow modulation [120]. As opposed to thermal modulators, valve-based modulators use a pneumatic system for modulation. No refrigerant and a low cost of a single analysis are the main advantages of the use of these modulators.

Cryogenic modulators are commonly used in scientific research. It results from the fact that they allow for the use of mass spectrometers. It also explains why only GC×GC-MS systems equipped with cryogenic modulators are available on the market. Cryogenic modulators are the most frequently used in food analysis include mostly LMCS modulators [18,61,121–130], dual-stage modulators [5,15,22,34,131–138] and loop modulators [26,27,80,139–146] (Figure 1).

The opinion of Tranchida seems correct that the ideal modulators should be a combination of the advantages of currently available modulators: the performance of cryogenic modulators, the simplicity of phase-ratio modulators and the production costs and easy-to-use operation of flow modulators [147]. Although currently manufactured modulators increasingly meet these requirements, the connection of all mentioned features is not practically feasible.

3. Mass spectrometry

3.1. *Characteristics of the detector used*

Mass spectrometers (MS) belong to the main elements of the GC×GC-MS and are used for detection and determination of chemical compounds eluting from the secondary chromatographic column. MS detectors combined with the GC×GC technique can be used for the analysis of food samples on condition that the key criterion is met. They must be characterised by a relatively fast data acquisition rate.
In the mid-1990s, in combination with the GC×GC technique, a flame ionisation detector (FID) was used, for which the data acquisition rate was 50-200 Hz [19,20,122,148–150] and the electron capture detector operates at a data acquisition rate of 50 Hz [26,27,125,151–153]. After 2004, MS detectors were more often used for the detection of chemical substances in food samples (Figure 2).

The MS detector is one of the most advanced analytical tools used for the detection and determination of volatile chemical substances. It allows for determining analytes in a broad range of concentrations differing in the range of 4 to 6 order of magnitude. The main advantage of these MS detectors is the high sensitivity of the device, which allows for detecting very small amount of chemical substances (in the amount of a few pg). The use of MS detectors allows for obtaining information about the chemical structure of detected analytes [154]. By comparing mass spectra obtained during research with spectra available in mass spectrum databases, it is possible to determine which substances are present in food on a preliminary basis. It is not possible if other detectors used in combination with GC that are used in food analysis.

Food analysis performed using the GC×GC-MS technique can be divided into two main groups: targeted and non-targeted tests [155] . Next, in non-targeted analyses, screening assays and tests in which the chemical profile of the sample is compared, i.e. the so-called fingerprint method. While using screening assays, it is necessary to use a mass spectrometer, as only this detector allows for preliminary identification of chemical compounds in previously untested samples. The GC×GC-MS technique allows for the assessment of food samples in terms of their authenticity, quality and safety of food (detection of contaminants in food).

The first non-targeted food tests using an MS detector were performed in 2002. The Mariott and Shellie et al. and Dalluge et al. used a mass spectrometer equipped with a quadrupole analyser [156,157]. Quadrupole (Q) analysers that are most frequently used in MS detectors are used for food analysis together with time-of-flight (TOF) analysers. There are also detectors that can contain a triple quadrupole analyser (QQQ) or a high-resolution time-of-flight analyser (HR-TOF). Figure 3 presents a comparison of the principles of operation of MS detectors equipped with various analysers of fragmentation ions.

The quadrupole analyser (Q) operates in a continuous manner and it can function in two modes: SCAN, i.e. the scanning mode in which a defined range of fragmentation ion mass measurement is used and in the SIM mode, i.e. the monitoring of a selected ion when the intensity of a selected ion in time is registered. The use of the SCAN mode allows for checking which chemical compounds are present in a given sample. Quadrupole analysers can achieve scanning rates of up to several thousand amu/s; however, the operation in the SCAN mode determines their relatively low sensitivity. For this reason, the SCAN mode is used for testing food matrices with a lower degree of complexity. In the SIM mode, on the other hand, the quadrupole analyser works with higher sensitivity [158]. In this case, the MS spectrometer can be used for identification and quantitative determination of chemical substances present in food. MS detectors can be also equipped with a triple quadrupole analyser (QQQ). It consists of two quadrupole mass analysers separated by a collision cell [159]. This analyser is characterised by unique scanning modes. The main one of these is the mode of monitoring selected fragmentation reactions (MRM/SRM Multiple/Selected Reaction Monitoring). It allows for identification of the analyte tested on the basis of fragmentation reaction, which contributes to an increase in the selectivity of measurement. Mass analysers work in a continuous manner, owing to which they filter ions with maximum efficiency. This allows for analyte identification in complex matrices. While using the MRM mode, a high value can be obtained for the parameter defined as the signal to noise proportion (S/N) [160], which allows for obtaining low values of the limit of detection and limit of quantification (LOD and LOQ). The QQQ analyser allows for obtaining more reliable results of quantitative determinations as compared to the results of a quadrupole analyser. However, other design solutions are available on the market that allow for a more detailed analysis of food samples, namely, MS detectors equipped with an analyser, including time-of-flight analysers. The method of operation of a time-of-flight analyser (TOF) differs from the method of operation of quadrupole analysers. TOF analysers operate in a periodic manner. The value of the mass to charge ratio (m/z) is calculated on the basis of the time of flight of the fragmentation ion from the ionisation source to the MCP device. The time of flight is a characteristic value, which allows for determining the accurate mass of a given fragmentation ion. A mass spectrometer of the TOF type is characterised by good resolution and an accurate mass measurement [161]. The obtained experimental data can be translated into useful analytical information, i.e. into summary formulas of identified chemical compounds. The MS spectrometer equipped with a TOF analyser can be used in both targeted and non-targeted tests. It is dedicated for the identification of substances in samples that have not been tested yet. The TOF-MS detectors can operate in two modes: high data acquisition rate (100-500 spectra/s) [162] or high resolution with accurate mass measurement [163]. The first mode is used for quantitative analysis while the high-resolution mode is used for qualitative analysis. Main advantages of TOF analysers include the possibility of fast data acquisition (the number of spectra read in a time unit is the highest as compared to the use of other MS analysers), a broad range of analysed masses, high sensitivity of these devices and the possibility of simultaneous detection of a large number of fragmentation ions [164]. The design elements used in TOF analysers, namely ion optics and reflectron (ion reflector), allow for adjustment of the spatial position of fragmentation ions characterised by the same value of the mass-to-charge ratio (m/z). In this way, the time of flight for ions of the same type is measured with higher accuracy. One set of the aforementioned design elements is usually used in TOF analysers. At the end of 2015 and 2016, a new HR-T spectrometer appeared on the market in which approx. 40 sets of the aforementioned design elements were used (Fig. 3, bottom part of figure). In this way, the flight pathway of fragmentation ions increased from 2 m to 40 m as compared to the spectrometer equipped with a classical TOF analyser. This technology and novel data acquisition system enables a resolution of 50,000 FWHM, mass accuracies lower than 1 $mg{\cdot}L^{-1}$ (or 1 $mg{\cdot}kg^{-1}$), and acquisition rates up to 200-500 spectra/s (it should be mentioned that previous technical solutions of HR-T spectrometers allowed for obtaining resolution of approx. 5000 FWHM). The goal to facilitate rich analyte finding and high-confidence analyte identification in foodstuffs was achieved. As this solution is very new, only a few studies have been published in the world, which present the use of GC×GC in combination with a HR-T mass spectrometer of this class. According to the author of this study, the use of an MS detector of this class will make it possible to take a completely new, more detailed approach to food samples.

The MS detector equipped with a TOF analyser is the only analyser available on the market that allows for data acquisition at a rate equal to 500 spectra/s. Despite this fact, the popularity of the use of quadrupole analysers is still growing, as they are cheaper to operate, the unit price is lower and they are characterised by smaller outer dimensions. However, if the price is not the deciding factor, the use of detectors equipped with a TOF analyser, in particular HR-T one, provides more reliable results in food testing [158].

3.2. *Future trends in detection and determination of analytes concentration in food matrices*

Food is a very complex matrix, which in many cases makes reliable analysis difficult, leading to the extensive use of standards. The identification in screening analysis often resembles looking for a needle in a haystack, which translates to an increase of the duration and cost of a single analysis. Curtailing the use of standards would also facilitate the implementation of automated analysis and reduction of the work-hours of highly qualified personnel, which are often the bottleneck of analytical laboratories.

There are two possible paths of future development of techniques the use of which would enable reliable and accurate preliminary identification of substances. In the first approach, the currently established techniques can be incrementally improved, particularly with developments in both the resolution and sensitivity of the detector, as is the case with the above-described HR-T. This can be achieved through optimization of the operating parameters of the analyser and through increasing the number of ion optics (reflectrons), thus increasing the time of flight of fragmentation ions. A sufficiently accurate measurement of the fragmentation ion’s mass will limit the ambiguity in identification. Conversely, new libraries of mass spectra could be developed, in which an additional parameter would be included, e.g. drift time in the case of ion mobility spectrometry (IMS) coupled with Q-TOF. This is, however, a difficult task, as the current libraries, such as NIST or WILEY, contain hundreds of thousands of mass spectra, and a comprehensive update would require a concerted effort of several analytical laboratories over many years.

The second approach might be focused on the development of direct quantitative capabilities (without the use of standards) besides qualitative analysis. This could be realised e.g. by introducing chromatographic separation prior to selected-ion flow-tube mass spectrometry SIFT-

MS or proton transfer reaction mass spectrometry PTR-MS detection, provided that the detector is capable of sufficiently accurate mass measurement, as is the case with devices equipped with a dual MCP. Such a solution would be particularly useful in the food industry, where particular analytes are targeted, as it would possibly eliminate the need to use standards and calibration curves. However, in many cases, food analysis involves screening, in which case proper identification capabilities are also required. In order to concurrently realise both qualitative and quantitative analysis, two detectors could be used in parallel, with the so-called hard (e.g. EI) and soft (e.g. PTR) ionisation, respectively.

4. Applications of two-dimensional gas chromatography coupled with mass spectrometry in food studies

The two-dimensional technique of gas chromatography coupled with mass spectrometry has numerous applications in food research. The majority of them can be classified as targeted analysis for food process monitoring, food freshness evaluation, food authenticity determination, assessment of contamination content and method optimisation (Table 2).

The GC×GC-MS is a useful tool for monitoring processes occurring in foodstuffs and during their production. Process monitoring using this technique was performed for wind samples. In 2010, this technique was first used to distinguish the degree of micro-oxygenation of wine [180]. Owing to the use of GC×GC-MS, it is also possible to follow changes in wine aroma at individual stages of production [169,183] and wines stored under specific conditions [194,195]. Vestner et al. studied the influence of malolactic fermentation on the composition of the volatile fraction of the Pinotage wine [176]. Robinson et al., on the other hand, tested the influence of using various yeast types on the aroma profile of Western Australian Cabernet Sauvignon wines during their production process [168]. The GC×GC-MS technique also proved useful for the investigation of microbial metabolism of Syrah grape phenolic compounds [184]. Two-dimensional gas chromatography coupled with mass spectrometry is a useful tool for controlling the process of thermal food processing. One example of the application of this technique is the study of the effect of heat treatment on the composition of butter samples [190] and poultry [7]. The influence of selected parameters used during the roasting process on the composition of the volatile fraction of foodstuffs was tested for hazelnuts [141], barley [20] and the Pistacia terebinthus fruit [181,187]. Using the GC×GC-MS technique, it is also possible to define the influence of the extraction methods used on the composition of the volatile fraction of the tested sample. Such research on olive oil samples was performed by Vaz-Freire et al. [67]. Also, analysis of Crambe abyssinica oil samples was performed to determine changes occurring in the composition of these samples, depending on the extraction technique used. The research conducted by Ozel et al. detailed the discrimination between essential oils from the leaves of *Thymbra spicata L.,* which were extracted using different parameters of subcritical water. The GC×GC-MS technique was used to determine the quality of drinking water after the disinfection process [144] and the quality of tea infusions prepared in various ways [53].

The use of the GC×GC-MS technique can be successfully used for the assessment of food freshness. Gögüs et al. determined the maturity of *Cheddar* cheese by analysing the composition of the volatile fraction of samples stored in a varying period of time [38]. Dairy products were also tested by Tranchidaa et al. Lipids in the unsaponifiable fraction of milk using a detector of the HR-TOFMS type were identified and determined. The use of the GC×GC-MS technique also allowed for determining fruit freshness. The comparison of the volatile composition of the fresh and post-harvested strawberry fruits was done. Also, untargeted analysis of apples was performed right after they were picked and after storing them for a specified period of time [198]. Similar research was conducted by Costa et al. for white truffle samples [80]. In 2003, the influence of the crystallisation process on the smell of ginger was also determined [147]. The GC×GC technique is also a useful tool for the determination of the influence of storage on the volatile sample composition of wine [136,139,200] and also other alcoholic beverages such as sake [178]. Leduc et al. determined odour-active chemical compounds that formed during the storage of sea bass fish [199]. Volatile fraction analysis allowed for identification of the aroma compounds of fennel seeds, leading to a shelf quality index [18].

Aroma profiling is a very important aspect in food analysis. In recent years, wines from various strains were tested by characterising volatile chemical compounds responsible for wine aroma [14,127,128,134,135]. Research was conducted on alcoholic beverages such as Chinese liquors [121] and ciders [239]. The GC×GC-MS technique is also an effective tool thanks to the application that allows for aroma profiling research for fruit samples. Profiling analysis of the volatile components derived from apples, pears and quince fruit was performed by Schmarr & Bernhardt [165]. On the other hand, in 2015, 3-methylbutan-1-ol, 3-methylbutan-1-ol acetate, 2-phenylethyl acetate and phenylethyl alcohol were classified as chemical compounds characteristic of bananas [238]. Owing to the use of the GC×GC-TOF-MS technique, it was also possible to determine quantitatively chemical compounds of the blueberry and physalis [236]. In the research of artichokes, 130 compounds were found, 109 of which were reported for the first time in *C. scolymus L* [142]. Breme et al. defined two chemical compounds with the highest odour impact in cress samples [243]. Cocoa beans were also analysed, which allowed for the identification and determination of 4 chemical compounds, determining the odour of these samples [245]. Three of the aforementioned chemical compounds were also found to be chocolate discriminants [248]. In 2004, using qMS and TOF-MS detectors, the composition of the volatile fraction of roasted coffee beans was characterized [203], while in 2013, quantitative headspace analysis of roasted hazelnuts was performed [246]. Purcaro et al. developed a method allowing for characterisation of the yerba mate (*Ilex paraguariensis*) volatile fraction using solid-phase microextraction and GC×GC-MS [241]. The GC×GC-MS technique was also used for aroma profiling of essential oils [156,237,244,250]. In oil samples from pyrolysis of sugar cane straw and its fractions, a total number of 331 compounds tentatively identified and 166 were confirmed [249]. In 2004, in turn, flavour analysis of olive oil was performed [149]. Owing to the use of the GC×GC-MS technique, also the aromatic profile of dairy products was determined, namely, dry milk powders [28] and dairy spread extract as well as dairy and non-dairy sour cream [251]. Analyses of the composition of the volatile fraction of orange juice were performed, and 10 odour-active compounds were identified [57]. Rochat et al. tested shrimps. They identified trimethylamine, 2-acetyl-1-pyrroline, and 2-ethyl-3,5-dimethyl pyrazine as the main odour-active compounds occurring in this food matrix [247]. The GC×GC-MS technique was used for aroma analysis of 9 herbs [171] and Malaysian soursop (*Analyte bariatric*) [22].

Some food research conducted using the GC×GC-MS technique concerns the optimisation of the selected parameter of the analytical method. The research conducted by Omar et al. was the optimisation of the GC × GC set-up to make possible the analysis of essential oils from rosemary and oregano [48]. Honeys were the subject of research during which optimization of the SPME method for the analysis of honey volatiles was performed [78]. In 2013, the analytical method for the identification and quantification of mineral-oil contaminants was optimised using two-dimensional gas chromatography [140]. The optimisation of the analytical method using GC×GC-MS was also performed to check the opportunities and limitations resulting from the use of the microextraction technique to the stationary phase for the analysis of apple samples [252].

The GC×GC-MS technique is also used for the assessment of the authenticity of food samples. It is usually used for the analysis of alcohol samples. In the case of wine samples, it is used for classification of samples according to various types caused, for example, by the use of different strains of grapes for production [166,167], or classification according to the various age [202] of samples and also to show differences between the various types of wines [36]. The technique above was also used for the classification of alcohols sample (spirits, vodkas, whisky, tequila and liqueurs) [209]. Honeys are another type of sample that is frequently analysed using the GC×GC-MS technique. The use of this technique allows for classification of samples according to their botanical [148,215] or geographic origin [173,215]. Cajka et al. distinguished honey samples from Corsica from honeys produced in other European countries. The aspect of authenticity assessment in the case of samples from Corsica is particularly important as the name of this region is protected [213]. Tests of samples of coffee beans, cocoa beans, nuts and spices are another example of research in which volatile fraction profiles were analysed. Cordero et al. analysed samples into samples of green coffee beans and roasted coffee beans [208] and distinguished between coffee samples according to their botanical origin [214]. Similar distinctions were made for samples of nuts: those were classifications into samples from various geographic regions [211] or of various botanical origin [214]. In the literature, one can also find information concerning research using cocoa beans. The aim of this research was to determine the place of origin of the samples (Brazil, Ivory Coast) [207]. For pepper grains, the main objective of the research was to develop a useful method for distinguishing between various varieties of these samples [212]. Cooking oils are another food matrix tested using GC×GC-MS. Oil samples were classified in terms of their botanical [172] and geographic origin [17] and also the assessment of the authenticity of olive oil, i.e. the detection of adulteration of extra virgin olive oil [69]. The GC×GC-MS technique is also a useful technique for research using fruit samples. Strawberry samples produced in Australia were distinguished according to their botanical origin [204], while pepper samples (*Capsicum spp.*) according to their cultivar [177]. Dynerski's et al., on the other hand, classified blueberry, cranberry and physalis samples [205]. For the first time, the content of pro-health ingredients of physalis fruits was compared with other berries. The GC×GC-MS technique was also used for the composition of selected herbs. An analytical method was developed during the research that made it possible to classify samples of basil [206], teas [170] and ginseng [210] according to their species. Schäffer et al., on the other hand, developed a method allowing for distinguishing samples of herbs contaminated and uncontaminated with substances from the leaves of the *Turnera diffusa* plant [9].

Another application of the GC×GC-MS technique is the assessment of the degree of contamination of food samples. Pesticides belong to the most frequent contaminants found in foodstuffs. Their presence is mostly tested in samples of vegetables [145,157] and fruits [10,59,150,222]. Pesticides can be also contained in plant materials. Reports appear in the literature concerning tests of tea samples [131,227] or oilseeds [25] in which pesticides were detected using GC×GC-MS. Hayward et al., in turn, described a method for determining pesticides and their metabolites in cow's milk and in cream [13]. The GC×GC-MS technique is very often used to characterize the aroma of wines. It is also employed for contaminant detection and, in particular, pyrazines [16,232,233]. These are chemical compounds that can be found in vegetables, nuts, spices and also in grapes and wines. The presence of these substances may cause an unpleasant odour and taste in wines. These compounds also occur in vegetables, which is why Lojzova et al. developed a method of pyrazine detection in potato chip samples [21]. The GC×GC-MS technique was used for the determination of organic contaminants mostly hydrocarbons. Organic contaminants were identified in fish oils [11] and in rice samples from a range of varieties [219]. The detection of organic contaminants from polycyclic aromatic hydrocarbons (PAHs) in the food is very important due to the fact that these substances exhibit carcinogenic properties. PAHs were identified in cooking oil samples [12,224] and also in grape samples and wines produced from the these grapes [226]. Apart from PAHs, dioxins and polychlorinated biphenyls (PCBs) are very harmful substances present in foods. Compounds belonging to these chemical classes are characterised by good solubility in fats, which is why they are often present in samples of animal origin, e.g. meat [5], fish and milk [8]. PCBs can also occur in other food matrices, e.g. in grapes and wines [226]. Another group of chemical compounds with a negative effect on the human body are benzenic and halogenated VOCs (BHVOCs). This group of chemical compounds also exhibits lipophilic properties. For this reason, Ratel et al. analysed the composition of meat products, milk and seafood [72]. Meat samples were also tested for sulphur compound content by Rochat’s et al. [220].

As mentioned above, owing to the coupling of the two-dimensional gas chromatography technique with mass spectrometry, it is possible to determine a broad spectrum of chemical compounds in food matrices. The use of the combination of these techniques allowed for identification and determination of disaccharides [216] and amino acids [218] in honeys and alcoholic beverages, flavonoids in chocolate samples [81] and also lipids in quinoa samples [231]. Also, ethyl carbamate in wine samples was detected [228], which is particularly important as this chemical compound is characterised by high toxicity and it may be generated during incorrect technological processes.

5. Conclusions

For the last 15 years, two-dimensional gas chromatography coupled with mass spectrometry has been successfully used in many areas of daily life, including food analysis. Due to high resolution, which translates to high peak capacity and above-average detection capabilities, its use enables the analysis of a wider range of complex matrices. Its application has led to the detailed characterization of many foodstuffs on a level previously unachievable. GC×GC has a great potential in the assessment of quality and authenticity of food. Moreover, the introduction of the second dimension facilitates the separation of the principal background noise from the analytes' signal, thus eliminating the necessity of sample preparation. Still, it remains less popular than one-dimensional gas chromatography, in part due to its complexity and high unit and operating costs, despite the recent developments, in particular in the miniaturization and simplification of modulators. The coupling of two-dimensional gas chromatography and mass spectrometry is necessary due to the shortcomings of the latter, namely insufficient resolving power and accuracy of mass spectrometers. However, recent developments in the construction of analysers, such as the introduction of HR-T, might in the future lead to a solution in which chromatographic separation will be redundant. The improved parameters of mass spectrometers, together with the development of mass spectra libraries, could at the same time reduce the need to use standards for qualitative analysis. The rapid developments in the field of modulators and MS detectors yield an increasing number of published works involving two-dimensional gas chromatography-mass spectrometry. Nevertheless, the number of studies is still relatively low considering the possible applications and potential of this technique. One can wonder if the coming year will bring any revolutionary developments in this area.

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Conflict of interest

No potential conflict of interest was reported by the author.

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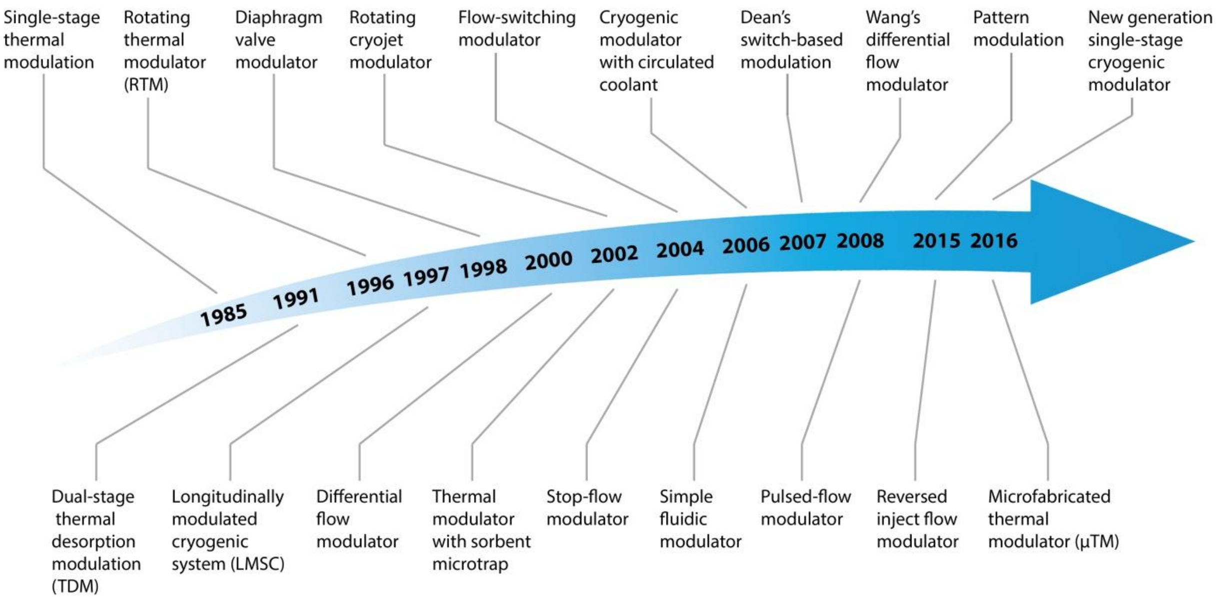

Fig 1. Development of modulators since their appearance.

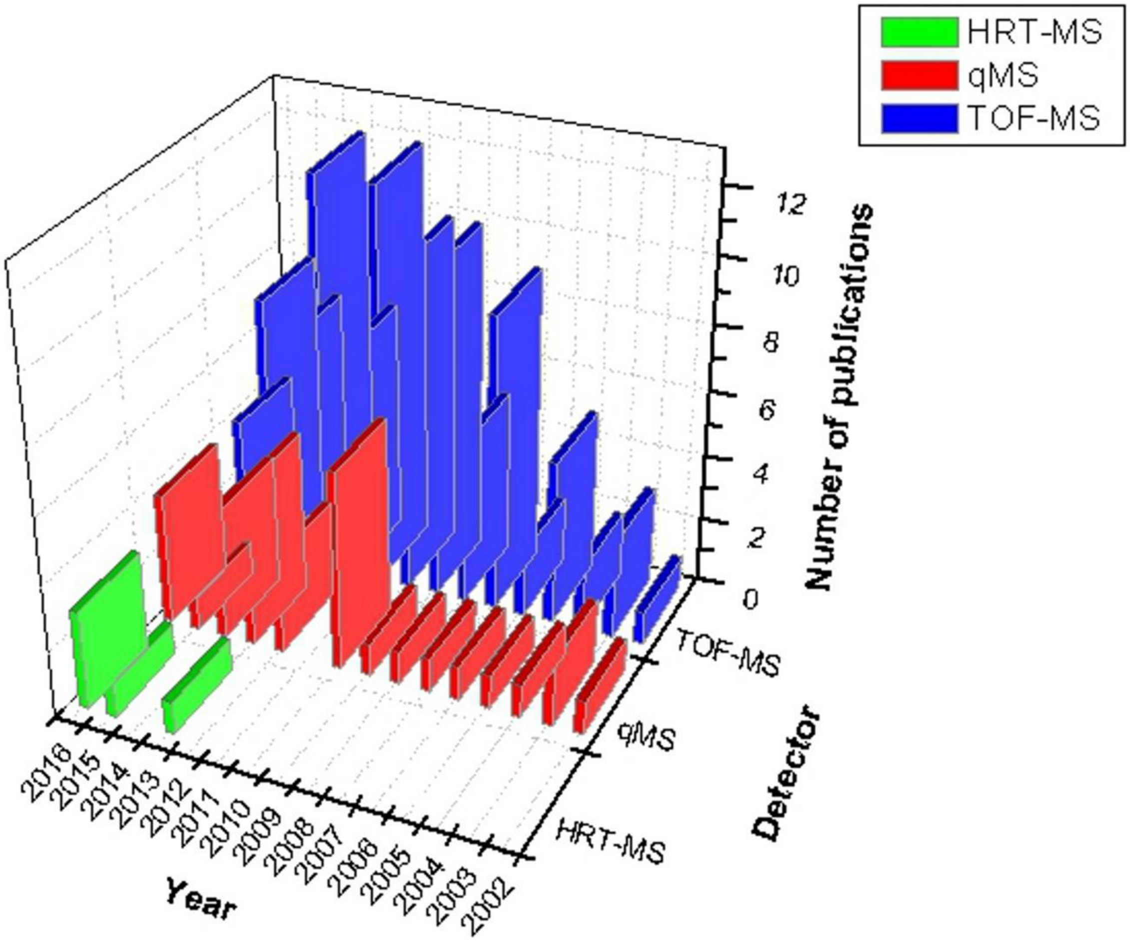

Fig 2. MS detectors used in combination with GC×GC.

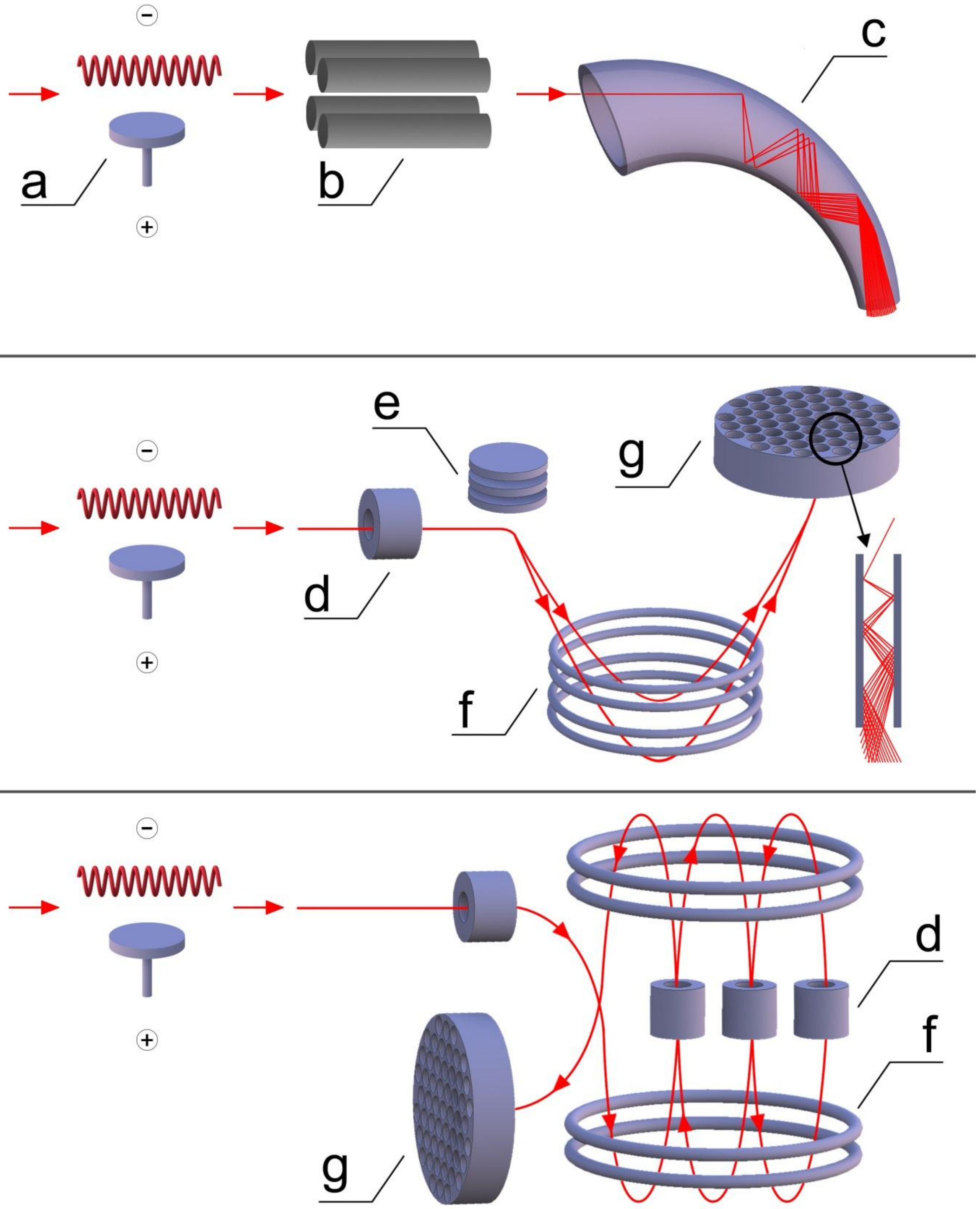
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Fig. 3. Comparison of the working principle of MS detectors equipped with quadrupole (top), time-of-flight (middle) and a high resolution time-of-flight analyser (bottom); a - source of ionisation (EI), q - quadrupole, c - dynode, d - ion optics, e - deflector plates, f - ion reflectors, g - microchannel plate (MCP).

Table 1. Comparison of the use of GC and GC×GC technique in terms of application in food analysis.

Technique Matrix	GC						GC×GC					
	Amount of chemical compounds	Time [min]	Chromatographic column	Oven temperature program	Carrier gas/flow	Ref.	Amount of chemical compounds	time [min]	Chromatographic column	Oven temperature program	Carrier gas/flow	Ref.
Alcoholic beverages												
Liquor Moutai	86	37	HP-INNOWAX (60 m × 0.25 mm × 0.25 m)	50°C – 250°C	He, 1.0 mL·min^{-1}	[30]	528	100	HP-Innowax; (60 m× 0.25 mm ×0.25 µm); DB-1701 (1.2 m× 0.1 mm ×0.4 µm)	50°C – 260°C	He, 1.3 mL·min^{-1}	[31]
African red wine	52	40	DB-WAX (60 m × 0.25 mm, 0.25 µm)	40°C – 200 °C	He, 1.0 mL·min^{-1}	[32]	276	84	Rxi 5Sil MS (30 m × 0.25 mm× 0.25 m), Rtx – PCB (0.8 m × 0.18 mm× 0.18 um)	35°C – 250°C	He, 1.0 mL·min^{-1}	[15]
Sparkling wine	33	126	SPB-1 (30 m × 0.25 mm × 0.25 µm)	40 °C – 250°C	He, 1.0 mL·min^{-1}	[33]	480	82	DB-WAX (30 m × 0.25 mm × 0.25 µm); DB-17 ms (1.70 m × 0.18 mm × 0.18µm)	35°C – 250°C	He, 1.0 mL·min^{-1}	[34]
White wine	16	118	BP-21 (50 m × 0.32 mm x 0.32m)	70°C – 190°C	He, 1.0 mL·min^{-1}	[35]	>800	80	VF-5MS (30 m x 0.25 mm x 0.25 µm; VF-17MS (1.65 m x 0.10 mm x 0.20 µm)	30°C – 240°C	He, 1.3 mL·min^{-1}	[36]

Dairy products												
Cheddar cheese	23	55	ZB-Wax (30 m × 0.25 mm × 1.0 µm)	40°C – 250°C	He, 1.0 mL·min^{-1}	[37]	57	45	DB5 (10 m × 0.18 mm × 60.18 µm); DB17 (1.6 m × 0.18 mm × 60.18 µm)	40°C – 250°C	He, n.d.	[38]
Milk	27	40	Silica capillary column (100 m × 0.25 mm × 0.39 µm)	60°C – 235°C	H2, 1.4 mL·min^{-1}	[39]	45	79	CP7420 (100 m × 60.25 mm × of 0.25); HP-5MS (1.5 m × 0.1 mm × 0.1)	170°C–250°C	He, 1.0 mL·min^{-1}	[40]
Dry milk	17	29	DB-WAX (50 m × 0.20 µm × 0.40 µm)	40°C – 260°C	He, 2.0 mL·min^{-1}	[41]	93	87	SolGel-Wax (30 m × 0.25 mm × 0.25 µm); OV1701 (1 m × 0.1 mm × 0.10 µm)	40°C – 250°C	He, 0.7 mL·min^{-1}	[42]
Cream	48	175	Rtx 2330 (100 m × 0.25 mm ×0.1 µm)	40°C – 210°C	He, 0.9 mL·min^{-1}	[43]	30	39	VF-5 (30 m × 0.25 mm × 0.25 µm); BPX-50 (1.5 m × 0.15 mm × 0.15 µm)	90°C – 290°C	He, n.d.	[13]
Spices												
Black pepper	22	24	Restek RTX-5 column (10 m × 0.18 mm × 0.25 µm)	40°C – 240°C	He, 0.5 mL·min^{-1}	[44]	>300	68	BPX5 (30 m × 0.25 mm ×0.25µm); BP20 (1.0 m × 0.1 mm× 0.1 µm).	35°C – 240°C	He, 1.3 mL·min^{-1}	[45]
Fennel	55	30	OV-1701 (30 m × 0.25 × 0.125 µm)	60°C – 180°C	He, 1.0 mL·min^{-1}	[46]	38	72	DB-FFAP (15 m × 0.25 mm × 0.25 µm); DB-1 (1.1 m × 0.1 mm × 0.1 µm)	50°C – 240°C	He, 0.7 mL·min^{-1}	[18]

Oregano	18	33	DB5-MS (30 m × 0.25 mm × 0.25 µm)	40°C – 250°C	He, 1.0 mL·min^{-1}	[47]	22	46	HP-5MS (30 m × 250 µm × 0.25 µm); DB-17MS (5 m × 250 µm × 0.25 µm)	60°C – 300°C	H_2, n.d.	[48]
Rosemary	25	47	SE 30 (10 m × 0.125 mm × 0.125 µm)	75°C – 220°C	Ni, 30 mL·min^{-1}	[49]	26	46	HP-5MS (30 m × 250 µm × 0.25 µm); DB-17MS (5 m × 250 µm × 0.25 µm)	60°C – 300°C	H_2, n.d.	[48]
Beverages												
Black tea	28	38	DB-5ms (25m x 0.25 mm x 0.25 mm)	82°C – 280°C	He, n.d.	[50]	36	23	BPX-5 column (40 m × 0.18 mm × 0.18 µm), SupelcoWax (2.5 m × 0.1 mm × 0.1 µm)	45°C – 260°C	He, 1.0 mL·min^{-1}	[51]
Green tea	39	13	Rtx®-5 (30 m length × 0.25 mm × 0.25 µm)	60°C – 250°C	He, 0.96 mL·min^{-1}	[52]	478	61	DB-5MS (30 m × 0.25 mm × 0.25 µm); DB-17HT (1.9 m × 0.1 mm × 0.10 µm)	60°C – 280°C	He, 1.0 mL·min^{-1}	[53]
Coffee	31	70	SGE SolGelwax (30 m × 0.25 mm × 0.25 µm)	40°C – 250°C	He, 2.0 mL·min^{-1}	[54]	50	128	Omegawax 250 (30 m × 0.25 mm, 0.25 µm), SLB-5ms (1.1 m × 0.05 mm, 0.05 µm)	60°C – 280°C	H_2, 50 mL·min^{-1}	[55]
Juice	49	56	HP-5 column (30 m × 0.25 mm × 0.25 µm)	40°C – 220°C	He, 1.0 mL·min^{-1}	[56]	13	69	HP-FFAP (30 m × 0.25 mm × 0.25 µm); Rxi-5sil MS (1 m × 0.18 mm × 0.81 µm)	40°C – 250°C	H_2, 1.5 mL·min^{-1}	[57]
Vegetables & Fruits												
Grape	27	25	DB-5ms column (30 m × 0.25 mm I.D., 0.1	70°C – 290°C	He, 1.0 mL·min^{-1}	[58	30	41	RTX-5MS (10 m × 0.18 mm × 0.2 µm), TR-50MS	70°C – 270°C	He, 1 mL·min^{-1}	[59

			m)			]			(1 m × 0.1 mm × 0.1 µm)			]
Strawberry	23	37	PTE5 (30 m × 0.32 mm × 0.25 µm)	40°C – 280°C	He, 1.5 mL·min^{-1}	[60]	21	48	EtTBS-β-CD (20 m × 0.25 mm × 0.25 µm); CycloSil B (26 m × 0.25 mm × 0.25 µm)	50°C – 240°C	H_2, 2.5 mL·min^{-1}	[61]
Orange	32	56	HP-5 column (30 m × 0.25 mm × 0.25 µm)	40°C – 220°C	He, 1.0 mL·min^{-1}	[56]	38	62	ZB-5 (30 m × 0.25 mm × 0.25 µm); BPX-50 (0.8 m × 0.10 mm × 0.10 µm)	60°C – 280°C	He, 0.8 mL·min^{-1}	[62]
Cucumber	100	17	HP-5 column (30 m × 0.25 mm × 0.25 µm)	-20°C – 220°C	He, 1.5 mL·min^{-1}	[63]	314	47	SolGel-Wax™, (30 m × 0.25 mm × 0.25 µm); RTX 17-01 (1.0 m × 0.1 mm × 0.1 µm)	40°C – 250°C	He, 1.3 mL·min^{-1}	[64]
Fats												
Vegetable oil	61	82	DB-Petro (50 m × 0.2 mm × 0.5 µm)	60°C – 260°C	He, 0.5 mL·min^{-1}	[65]	700	82	DB-Petro (50 m × 0.2 mm × 0.5 µm); DB-17ht (2.6 m × 0.1 mm × 0.1 µm)	60°C – 260 °C	He, 0.5 mL·min^{-1}	[65]
Olive oil	52	30	BPX5 (50 m×0.25 mm × 0.25 µm)	50°C – 300°C	He, 1.2 mL·min^{-1}	[66]	102	74	BPX5 (30 m × 0.25 mm × 0.25 µm); BPX20 (1.5 m × 0.1 mm × 0.1 µm)	35°C – 240°C	He, 1.3 mL·min^{-1}	[67]
Extr	45	7	ZB-WAX	40°C	He,		256	7	Rxi-5ms	40°C	He,	

a virgin olive oil		0	(60 m × 0.32 mm × 0.50 µm)	– 250°C	2.0 mL·min^{-1}	[68]		4	(30 m × 0.25 mm × 0.50 µm); Supelcowax-10 (1.2 m × 0.1 mm × 0.10 µm)	– 320°C	0.7 mL·min^{-1}	[69]
Butter	23	28	DB-1 (50 m×0.32 mm ×1 µm)	50°C – 280°C	He, 1.5 ml·min^{-1}	[70]	40	77	Supelcowax-10 (30 m × 0.25 mm × 0.25 µm); SPB-5 (1 m × 0.10 mm × 0.10 µm)	50°C - 280°C	H$_2$, 2.0 mL·min^{-1}	[71]
Meat & Fish												
Chicken	44	44	DB-Wax (30 m × 250 µm × 0.25 µm)	40°C - 250°C	n.d.	[7]	95	78	DB-1 (10 m × 0.25 mm × 0.25 µm); BPX-50 (1 m × 0.1 mm × 0.1 µm)	40°C - 250°C	n.d.	[7]
Lamb	11	73	DB-5, (60 m × 0.32 mm × 1 µm)	40°C - 230°C	He, 1.0 mL·min^{-1}	[72]	81	79	DB-5 (30 m × 0.25 mm × 0.25 µm); DB-17 (2 m × 0.1 mm × 0.1 µm)	40°C - 230°C	He, 1.0 mL·min^{-1}	[72]
Beef	17	60	SP 2331 (60 m × 0.32 mm × 0.2 µm)	120°C - 260°C	He, 0.8 mL·min^{-1}	[73]	206	73	Rtx-Dioxin2 (60 m × 0.25 mm × 0.25 µm); BPX-50 (2 m × 0.1 mm × 0.1 µm)	90°C - 320°C	He, 1.5 mL·min^{-1}	[74]
Salmon	19	79	CP-Sil 8 CB (30 m × 0.25 mm × 0.25 µm)	80°C - 300°C	He, n.d.	[75]	44	58	Rtx-5Sil-MS (15 m × 0.25 mm × 0.25 µm); DB-17MS (2 m × 0.18 mm × 0.18 µm)	60°C - 300°C	He, 1.0 mL·min^{-1}	[76]
Others												
Honey	86	47	HP-5MS (30 m x 0.25	40°C –	He, 0.9	[	164	54	30 m60.25 mm id60.25 lm	45°C –	He, 1.3	[

			mm x 0.25 µm)	250°C	mL·min^{-1}	77]			film thickness DB-5ms column coupled to a 1.25 m60.10 mm id60.10 lm film DB-5ms (30 m × 0.25 mm × 0.25 µm); SUPELCOWAX 10 (1.25 m × 0.1 mm × 0.1 µm)	280°C	mL·min^{-1}	78]
White truffle	20	57	EC-WAX (30 m × 0.25 mm × 0.25 µm)	35°C – 190°C	He, 1.5 mL·min^{-1}	[79]	80	80	SLB-5 ms (30 m × 0.25 mm × 0.25 µm); Supelcowax-10 (1.25 ×0.10 mm × 0.10 µm)	40°C – 280 °C	He, 1.0 mL·min^{-1}	[80]
Dark chocolate	3	37	HP-5ms (30 m × 0.25 mm × 0.25 µm)	100°C–310°C	He, 1.5 mL·min^{-1}	[81]	34	54	BPX5 (30 m × 0.25 mm × 0.25 µm); BPX50 (1.0 m × 0.1 mm × 0.1 µm)	100°C–310°C	He, 1.2 mL·min^{-1}	[81]
Hazelnut	47	42	CP-Wax 52 (60 m × 0.25 mm × 0.25µm)	40°C – 155°C	He, 1.0 mL·min^{-1}	[82]	79	90	CW20 (30 m × 0.25 mm × 0.25 µm); OV1701 (1 m × 0.1 mm × 0.10 µm)	50°C – 260°C	He, 1.0 mL·min^{-1}	[83]

Table 2. Application of GC×GC-MS techniques in food analysis.

No.	Type of matrix	Object of study	Sampling technique	Type of analysis	Data processing	Detector type	Modulator type	Year	Ref.
FOOD PROCESS MONITORING									
1	Wines	Discrimination between wine microoxygenation stages	HS-SPME	quantitative/ targeted	MSL	qMS	cryogenic	2010	[180]
2	Pistacia terebinthus fruit	Investigate the effects of different roasting methods on volatile components of P. terebinthus fruit	DTD	quantitative/ targeted	MSL, KI	TOF-MS	cryogenic, a jet-type	2014	[181]
3	Crambe abyssinica	The study of the chemical composition of the vegetable oil obtained from C. abyssinica with the following	DTD	semi-quantitative/ targeted	MSL	TOF-MS	cryogenic, liquid nitrogen quad-jet	2014	[182]

		three extraction processes							
4	Tea	Quality classification	SDE	qualitative/ untargeted	MSL, KI	TOF-MS	cryogenic, liquid nitrogen quad-jet	2016	[53]
5	Wines	Investigation of the main changes in the volatile profile of sparkling wines during their production	HS-SPME	semi-quantitative/untergeted	MSL, KI, FA, HCA	TOF-MS	thermal, quad-jet dual stage	2014	[169]
6	Wines	Investigation the main changes in aroma of Moscatel sparkling wines during vinification	HS-SPME	quantitative/ targeted	MSL, KI	TOF-MS	thermal, non-moving quad-jet dual stage	2015	[183]
7	Wines	Investigation the role of yeast, canopy, and site on the composition and sensory characteristics of Western Australian Cabernet Sauvignon wines	HS-SPME	qualitative/ untargeted	MSL, KI, PCA	TOF-MS	cryogenic, liquid nitrogen quad-jet	2011	[168]
8	Hazelnuts	Discrimination between	HS-SPME	qualitative/ untargeted	MSL	qMS	thermal,	2012	[14

		different roasting time of hazelnuts					cooled-loop		1]
9	Water	Identification of volatile and semi-volatile DBPs (disinfection by-products) in drinking water	SPE	qualitative/ untargeted	MSL	qMS	thermal, cooled-loop	2016	[144]
10	Wines	Investigation of microbial metabolism of Syrah grape phenolic compounds	SPE	qualitative/ targeted	MSL	TOF-MS	cryogenic, liquid nitrogen quad-jet	2013	[184]
11	Brazilian chamomile (Matricaria recutita L.)	Study the impact of the agricultural practices of M. recutita L. on the occurrence of sesquiterpenic compounds	HS-SPME	qualitative/ untargeted	MSL, KI	TOF-MS	cryogenic, quad-jet dual stage	2011	[185]
12	Chicken meat	Detection of volatiles in processed chicken meat	ASE-SAFE	qualitative/ untargeted	MSL	HR-T	thermal, cooled-loop	2015	[7]
13	Metabolites of Methylobacterium extorquens	Determination of targeted metabolites involved in central carbon metabolism	SPE	qualitative/ untargeted	MSL	TOF-MS	cryogenic, quad-jet dual stage	2009	[186]

14	Pistacia terebinthus fruit	Examination the effect of roasting time on the volatile components of P. terebinthus fruit	DTD	qualitative/ untargeted	MSL, KI	TOF-MS	cryogenic, quad-jet dual stage	2011	[187]
15	Ziziphora taurica subsp. taurica	Comparing different methods of isolation the volatile components from the leaves of Ziziphora taurica subsp. taurica	SD, SWE, SPE	qualitative/ untargeted	MSL	TOF-MS	cryogenic	2005	[188]
16	Cacao beans	Assessment of the impact of moisture on cacao beans	HS-SPME	quantitative/ targeted	MSL	TOF-MS	thermal	2010	[189]
17	Butter	Study the effect of heat treatment on the composition of butter samples	HS-SPME, SPE	quantitative/ targeted	MSL	TOF-MS, FID	cryogenic, quad-jet dual stage	2005	[190]
18	Cachaça	Study of cachaça production	HS-SPME	qualitative/ untargeted	MSL	TOF-MS	cryogenic	2009	[191]
19	Cachaça	Analysis samples after the fermentation process and after ageing of different wood	HS-SPME	qualitative/ untargeted	MSL	TOF-MS	cryogenic, LMCS	2008	[192]

		materials							
20	Eucalyptus	Differentiation between susceptible and non-susceptible (on rust disease) clones of Eucalyptus	HS-SPME	qualitative/ untargeted	MSL	qMS	cryogenic	2013	[193]
21	Wines	Investigation of the impact of malolactic fermentation (MLF) on the volatile composition of Pinotage wines	HS-SPME	quantitative/untargeted	PCA	TOF-MS	cryogenic	2011	[176]
22	Olive oils	Classification of the olive oils dependently of the treatment used (extraction method)	HS-SPME	qualitative/ targeted	PCA, ANOVA	TOF-MS	cryogenic	2009	[67]
23	Eucalyptus	Determination disease markers in Eucalyptus plants	HS-SPME	qualitative/ untargeted	MSL, U-PLS-DA, OSC	qMS	cryogenic , two-stage	2013	[179]
24	Wines	Classification wines stored in bottles for 6 months	HS-SPME	qualitative/ untargeted	MSL	TOF-MS	cryogenic, quad-jet	2013	[194]

		at different temperatures					dual stage		
25	Wines	Analysis of Nebbiolo-based wine volatiles, aged in oak wood barrels for 18 months at constant temperature	HS-SPME	qualitative/ untargeted	MSL	TOF-MS	cryogenic, quad-jet dual stage	2014	[195]
26	Essential oils	Discrimination between essential oils from the leaves of Thymbra spicata L. which were extracted using different parameters of subcritical water	SPE, SWE	qualitative/ untargeted	MSL	TOF-MS	cryogenic, quad-jet dual stage	2003	[196]
FOOD FRESHNESS EVALUATION									
27	Cheddar cheeses	Discrimination between stages of maturity of Cheddar cheeses	DTD	semi-quantitative/untargeted	MSL	TOF-MS	cryogenic	2006	[38]
28	Strawberries	Comparion the volatile composition of the fresh and post-harvested fruits	HS-SPME	semi-quantitative/ targeted	RT and confirmation with standards, PCA		LMCS	2005	[23]

29	Dairy products	Qualitative and quantitative analysis of the unsaponifiable fraction of milk lipids (cow butter, buffalo, ewe, and goat milks)	HS-SPME	qualitative/ targeted	MSL	HR-T	cryogenic, quad-jet dual stage	2013	[197]
30	Ginger	Comparison the fresh ginger with a crystallized ginger sweet	HS-SPME	qualitative/ untargeted	MSL	FID	cryogenic	2003	[146]
31	Apples	Metabolite profiling of apples	HS-SPME	qualitative/ untargeted	MSL	TOF-MS	cryogenic, quad-jet dual stage	2012	[198]
32	White truffles	Assessment of influenced by storage conditions on freshness of white truffles	HS-SPME	quantitative/ targeted	MSL, PCA	FID/qMS	cryogenic, quad-jet dual stage	2015	[80]
33	Wines	Analyzis of the composition of Marsala wine (four sample-types of different ageing)	HS-SPME	qualitative/ untargeted	MSL	FID/qMS	cryogenic, quad-jet dual stage	2014	[139]
34	Sake	Exploration of relationship between the chemical	HS-SPME	qualitative/ targeted	PCA, ANOVA	TOF-MS	cryogenic, quad-jet	2016	[178]

		components in sake and quality					dual stage		
35	Seabass	Identification of odorous compounds of European seabass (Dicentrarchus labrax) after 1, 4 and 15 days of storage	HS-SPME	qualitative/untargeted	MSL, RT and confirmation with standards	gMS	cryogenic	2012	[199]
36	Wines	Analysis of 2-aminoacetophenone in wine	HS-SPME	qualitative/targeted	MSL	qqMS	H/C MDGC	2016	[200]
37	Fennel seeds	Identification the aroma compounds, leading to a shelf quality index	HS-SPME	qualitative/untargeted	MSL	FID/TOF-MS	LMCS	2013	[18]
38	Wines	Evaluation in differences in sparkling wines from six different vintages and 48 wineries	HS-SPME	qualitative/untargeted	MSL	TOF-MS	thermal, non-moving quad-jet dual stage	2016	[136]
FOOD AUTHENTICITY ASSESMENT									
39	Herbs	Authentication and quality control of herbal products	HS-SPME	qualitative/untargeted	MSL	FID	thermal, non-moving quad-jet dual stage	2004	[148]
40	Honey	Discrimination between botanical	HS-SPME	qualitative/untargeted	MSL	TOF-MS	thermal, non-moving	2012	[201]

		origin of honey					quad-jet dual stage		
41	Wines	Classification of different aged wines	HS-SPME	semi-quantitative/ targeted	MSL, KI	TOF-MS	cryogenic, quad-jet dual stage	2011	[202]
42	Coffee beans	Assessment of quality and the detection of adulterations for roasted coffee beans	HS-SPME	qualitative/ targeted	MSL	FID	LMCS	2004	[203]
43	Agrostis stolonifera, Pennisetum clandestinum, Eucalyptus leucoxylon and Trifolium repens	Discrimination between different plant materials	HS-SPME	qualitative/ untargeted	MSL, KI	FID	cryogenic	2002	[19]
44	Australian-grown strawberry	Discrimination between botanical origin of strawberry	HS-SPME	quantitative/ tareted	MSL, RT and confirmation with standards	TOF-MS	cryogenic	2013	[204]
45	Edible oils	Discrimination between botanical origin of edible oils	HS-SPME	quantitative/ targeted	MSL, KI, PCA	TOF-MS	cryogenic	2014	[172]

46	Gooseberries, blueberries and cranberries	Discrimination the differences among the berries samples' compositions	HS-SPME	quantitative/ targeted	MSL, KI	TOF-MS	cryogenic	2016	[205]
47	Basil	Differentation between five cultivars of basil	HS-SPME	qualitative/ untargeted	MSL	TOF-MS	cryogenic	2008	[206]
48	Wines	Classification of five type of wines	HS-SPME	qualitative/ targeted	MSL, KI, PCA, LSDA	TOF-MS	thermal, non-moving quad-jet dual stage	2013	[166]
49	Wines	Classification of 3 Cabernet Sauvignon wines from Australia	HS-SPME	qaulitative/ untargeted	MSL, PCA	TOF-MS	cryogenic	2011	[167]
50	Cocoa nibs	Differentiation between cocoa nibs from Brazil and Ivory Coast	HS-SPME	qualitative/ untargeted	PCA	FID/qMS	cryogenic	2016	[207]
51	Coffee	Classification of Arabica green and roasted coffee	HS-SPME	semi-quantitative/ targeted	MSL, RT and confirmation with standards	qMS	thermal, cooled-loop	2010	[208]
52	Honeys	Discrimination between geographical origin of honey	HS-SPME	qualitative/ targeted	MSL, KI, LDA, DPLS, SIMCA and SV	TOF-MS	cryogenic	2010	[173]

					M				
53	Green, oolong and black teas	Classification of three type of teas	SDE	quantitative/ targeted	MSL, PCA, Heat map and HCA	TOF-MS	cryogenic	2013	[170]
54	Spirits	Classification of different type of spirits	HS-SPME	qualitative/ untargeted	MSL	TOF-MS	cryogenic	2009	[209]
55	Extracts of the roots of Panax (ginseng)	Investigation of different species of Panax (ginseng)	Soxlet	qualitative/ untargeted	MSL	qMS	LMCS	2003	[210]
56	Oils	Detection of aduleration in olive oil and hazelnut oil	HS-SPME	qualitative/ untargeted	MSL	FID	thermal	2006	[150]
57	Hazelnuts	Discrimination between geographical origin of roasted hazelnuts	SAFE HS-SPME	qualitative/ untageted	MSL	qMS	thermal	2010	[211]
58	Wines	Assess compositional differences in the wine volatile profile	HS-SPME	qualitative/ untargeted	MSL	TOF-MS	cryogenic	2011	[36]
59	Pepper	Analyzis of 13 pepper samples of different species	HS-SPME	qualitative/ untargeted	MSL	FID, qMS, TOF-MS	LMCS	2006	[212]
60	Olive oils	Discrimination between geographical origin of olive	HS-SPME	qualitative/ untargeted	MSL, PCA	TOF-MS	cryogenic	2010	[17]

		oils							
61	Honeys	Confirmation the authenticity of the honeys labelled as “Corsica”	HS-SPME	qualitative/ untargeted	MSL, PCA	TOF-MS	cryogenic	2009	[213]
62	Olive oils	Classification of olive oils correlated to the product sensory quality	HS-SPME	semi-quantitative/ targeted	MSL, PLS-DA, PCA, OPLS-DA	TOF-MS	cryogenic	2014	[69]
63	Peppers	Separation 3 types of peppers samples according to their aromas	HS-SPME	qualitative/ untageted	MSL, KI	TOF-MS	cryogenic	2015	[177]
64	Herbal highs	Analysis of the chemical signature of damiana for its identification in different herbal blends	UAE	qualitative/ untargeted	MSL, PCA	TOF-MS	cryogenic, quad-jet dual stage	2013	[9]
65	Coffee and hazelnuts	Discrimination between botanical origin of roasted coffee and hazelnuts	HS-SPME	qualitative	MSL	qMS	thermal, non-moving quad-jet dual stage	2008	[214]
66	Honeys	Discrimination between botanical and geographical origin of honey	HS-SPME	qualitative/ untargeted	RT and confirmation with standards	TOF-MS	cryogenic	2013	[215]

67	Standards	Analyzis of pesticides in food	HS-SPME	quantitative/ targeted	KI	ECD/FPD	cryogenic	1983	[151]
CONTAMINATION ASSESEMENT									
68	Milk and cheese	Separation of the 19 chiral polychlorinated biphenyls (PCB) in food samples (milk and cheese)	MSPD	qualitative/ targeted	RT and confirmation with standards	ECD	cryogenic	2005	[26]
69	Honey	Analysis of complex mixtures of disaccharides in honey samples	LLE	qualitative/ targeted	MSL, KI	TOF-MS	thermal, non-moving quad-jet dual stage	2010	[216]
70	Vegetable extracts	Determination of pesticides in extracts of carrots and celeriac	LLE	quantitative/ targeted	MSL, KI	TOF-MS	cryogenic	2002	[157]
71	Berries	Identification and quantification of terpenes in blue honeysuckle berry samples	HS-SPME	quantitative/ targeted	MSL, KI	TOF-MS	cryogenic	2014	[217]
72	Dark chocolate, propolis, and chrysanthem-um	Identification of flavonoids in dark chocolate, propolis, and chrysanthemum	HS-SPME	quantitative/ targeted	MSL	qMS, FID, TOF-MS	LMCS	2010	[81]

73	Wines, beers, honeys	Analysis of amino acids in wine, beer and honey	SPE	quantitative/ targeted	MSL	TOF-MS	LMCS	2005	[218]
74	Fish oils	Analyzis organic contaminants in fish oil	SPE	qualitative/ targeted	MSL	TOF-MS	cryogenic, dual jet	2009	[11]
75	Rice	Characterization of hydrocarbons contaminating food	SPE	qualitative/ targeted	MSL	TOF-MS	cryogenic, dual jet	2015	[219]
76	Cooked meat	Determination of process-induced toxicants and odorants in food	ASE	quantitative/ targeted	MSL, PCA	TOF-MS	cryogenic, dual jet	2015	[6]
77	Vegetables	Quantitation of fungicides in vegetable samples	LLE	quantitative/ targeted	MSL	NPD/ ECD	LMCS	2006	[129]
78	Roast beef	Detection of sulfur compounds in roast beef	HS-SPME	qualitative/ targeted	MSL	TOF-MS/O	cryogenic	2007	[220]
79	Milk, cheese, salmon	Detection of PCBs in food samples	SPE	qualitative/ targeted	MSL	ECD	thermal, cooled-loop	2005	[27]
80	Grapes	Determination of pyrethroid pesticides in grape samples	LLE	quantitative/ targeted	MSL	FID/ECD	thermal, cooled-loop	2009	[221]
81	Apple juice	Analysis of 24 residual pesticides in apple juice	DLLME	quantitative/ targeted	MSL	qMS	cryogenic	2009	[10]

82	Standards	Analysis polychlorinated biphenyls (PCBs) in food	HVD	qualitative/targeted	MSL	qMS	cryogenic	2005	[158]
83	Tomato	Identification of pesticide in tomato samples	HS-SPME	quantitative/targeted	MSL	qMS	thermal, cooled-loop	2012	[145]
84	Grapefruits	Analysis of trace-amount pesticides in red grapefruits	HS-SPME	quantitative/targeted	MSL	qMS	thermal, cooled-loop	2007	[222]
85	Fruits	Determination of pesticides residues in fruit samples	HS-SPME	qualitative/targeted	MSL	TOF-MS	cryogenic	2003	[223]
86	Meat	Analyzis of dioxin-related micropollutants in complex food matrices	ASE, GPC	quantitative/targeted	MSL	TOF-MS	cryogenic, dual jet	2015	[5]
87	Oils	Determination of polycyclic aromatic hydrocarbons in vegetable oils	HS-SPME	quantitative/targeted	MSL	TOF-MS	LMCS	2007	[224]
88	Grapes	Determination the monoterpenoid profile of grapes	HS-SPME	qualitative/untargeted	MSL	TOF-MS	cryogenic, dual jet	2007	[225]
89	Grapes and wines	Analysis of 160 pesticides, 12 dioxin-like polychlorinated biphenyls (PCBs), 12 polyaromatic hydrocarbons (PAHs)	DSPE	quantitative/targeted	MSL	TOF-MS	cryogenic	2010	[226]

		and bisphenol A in grape and wine							
90	Fish, pork, and cow's milk	Measurement of seven 2,3,7,8-substituted polychlorinated dibenzo-p-dioxins (PCDDs), ten 2,3,7,8-substituted polychlorinated dibenzofurans (PCDFs), four non-ortho-polychlorinated biphenyls (PCBs), eight mono-ortho-PCBs, and six indicator PCBs in foodstuff samples	PLE, LLE	quantitative/ targeted	MSL	TOF-MS	cryogenic, dual jet	2005	[8]
91	Grapes	Analysis of pesticides in grapes	DSPE	quantitative/ targeted	MSL	TOF-MS	thermal, non-moving quad-jet dual stage	2008	[59]
92	Chips	Analysis of substituted pyrazines and related substances in potato chips	HS-SPME	quantitative/ targeted	MSL	TOF-MS	cryogenic, dual jet	2009	[21]

93	Green tea extracts	Analysis of 423 pesticides, isomers, and pesticide metabolites in green tea (Camellia sinensis) extract	QuEChERS	quantitative/ targeted	MSL	TOF-MS	cryogenic, dual jet	2015	[227]
94	Milk and cream	Analyzis of pesticides and their metabolites including most of the persistent organic pollutants (POPs) in milk and cream	SPE	quantitative/ targeted	MSL	TOF-MS	cryogenic, dual jet	2010	[13]
95	Oil seeds	Screening of 68 pesticide residues (PRs) in peanut, soybean, rape seed, sesame, and sunflower seed	MSPD	quantitative/ targeted	MSL, RT and confirmation with standards	TOF-MS	cryogenic, dual jet	2012	[25]
96	Eucalyptus	Analysis of biogenic volatile organic compounds (BVOC) of 14 Eucalyptus clones	HS-SPME	qualitative/ untargeted	MSL, KI, CA, PCA	qMS	thermal	2003	[174]
97	Cods	Separation of polychlorinated biphenyl congeners	HS-SPME	qualitative/ targeted	MSL	ECD	thermal	2002	[152]

98	Wines	Identification and quantification of the toxic contaminant ethyl carbamate (EC) directly in fortified wines	HS-SPME	quantitative/targeted	MSL	TOF-MS	cryogenic, dual jet	2010	[228]
99	Wines	Determination of methoxypyrazines in wine	HS-SPME	quantitative/targeted	MSL	TOF-MS	cryogenic	2005	[16]
100	Lamb, milk, oysters	Determination the occurrence, risk for human health and entryways of benzenic and halogenated VOCs (BHVOCs) in meat products, milks and sea foods	HS-SPME	qualitative/untargeted	MSL	TOF-MS	cryogenic	2009	[72]
101	Grapes and wines	Analyzis of phenolic compounds in grapes and wines	HS-SPME	quantitative/targeted	MSL	FID	cryogenic	2009	[229]
102	Edible oils	Characterisation of fatty acids in fish and vegetable oils	HS-SPME	qualitative/unatrgeted	MSL	FID	cryogenic	2001	[230]
103	Rice,mung bean, snake bean and celery were	Analysis of 16 organophosphorus pesticides (OPs) in food	HS-SPME	quantitative/targeted	MSL	FPD	LMCS	2013	[130]

		matrices							
104	Quinoa seeds	Characterization of lipids in Quinoa seed (Chenopodium quinoa)	HS-SPME	quantitative/targeted	MSL	HR-T	cryogenic	2015	[231]
105	Fish oil from herring, spiked cows' milk, vegetable oil and an eel extract	Analysis of polychlorinated dibenzo-*p*-dioxins, dibenzofurans and WHO polychlorinated biphenyls in food	HS-SPME	quantitative/targeted	MSL	ECD	LMCS	2004	[125]
106	Rices and fish fat	Determination of organochlorine pesticide residues in rice and fish fat	SPE	quantitative/targeted	MSL	ECD	LMCS	2007	[153]
107	Wines	Quantitative analysis of four methoxypyrazines in white and red wine	HS-SPME	quantitative/targeted	MSL	qMS	cryogenic	2014	[232]
108	Wines	Determination of 3-alkyl-2-methoxypyrazines in grape must and wine	HS-SPME, SPE	quantitative/targeted	MSL	qMS	cryogenic	2010	[233]
109	Teas	Determination of multiple pesticide residues in tea samples	HS-SPME	quantitative/targeted	MSL	TOF-MS	cryogenic, dual jet	2008	[131]

110	Fish oils	Analytical screening method for 17 polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs) and 4 non-ortho polychlorinated biphenyls (PCBs) in fish oil	SPE	quantitative/ targeted	MSL	TOF-MS	cryogenic, dual jet	2008	[234]
111	Standards	Analysis of a large number of organic contaminants and residues at trace levels in food samples	HS-SPME, SPE	qualitative/ targeted	MSL	TOF-MS	cryogenic, dual jet	2011	[235]
112	Vegetable oils	Analysis of polycyclic aromatic hydrocarbons in vegetable oils	SPE	quntative/ targeted	MSL	TOF-MS	cryogenic, dual jet	2013	[12]
AROMA PROFILINGS									

113	Merlot wines	A qualitative characterization of volatiles of Merlot wines	HS-SPME	qualitative/ untargeted	MSL	TOF-MS	thermal, non-moving quad-jet dual stage	2012	[134]
114	Dry milk powders	Qualitatively and quantitatively screening volatiles and semi-volatiles of dry milk powders	HS-SPME, SBSE	qualitative/ untargeted	MSL	qMS	thermal, non-moving quad-jet dual stage	2013	[28]
115	Apples, pears, and quince fruit	Profiling analysis of the volatile components derived from fruit	HS-SPME	qaulitative/ untargeted	ANOVA, PCA	qMS	cryogenic	2010	[165]
116	Wines	Research on the chemical composition of Pinotage wines	HS-SPME	qualitative/ untargeted	MSL, KI	TOF-MS	cryogenic	2011	[14]
117	Gooseberry and blueberry	Comparison of the composition of the volatile fractions of Cape gooseberry and blueberry	HS-SPME	quantitative/ targeted	MSL, KI	TOF-MS	cryogenic	2015	[236]
118	Orange juice	Identify the compounds of major importance for the aroma of orange juice	HS-SPME	qualitative/ targeted	MSL, KI	TOF-MS	cryogenic	2015	[57]

119	Wines	Characterization of volatile compounds in South African wines	SPE	qualitative/ untargeted	MSL	TOF-MS	thermal, non-moving quad-jet dual stage	2011	[15]
120	Essential oils of Piperaceae	Comparison GC–qMS and GC × GC–qMS analyses for the essential oils of two species from the Piperaceae family, Manekia obtusa (Miq.) Arias, Callejas and Bornstein and Piper cubataonum C. DC.	LLE	quantitatie/ targeted	MSL	qMS	cryogenic	2014	[237]
121	Banana	Study to major aroma compounds in banana	HS-SPME	qualitative/ untargeted	MSL, KI	FID, qMS/O	cryogenic	2015	[238]
122	Ciders	Analysis of the odourant profile of ciders	HS-SPME	qualitative/ untergeted	MSL	TOF-MS	cryogenic	2012	[239]
123	Vanilla, olive oil	Flavour analysis in food samples	HVD	quantitative/ targeted	MSL	FID, TOF-MS	thermal, non-moving quad-jet dual stage	2004	[149]
124	Honey	Identification of the volatile fraction of the	HS-SPME	qualitative/ untargeted	MSL	FID, TOF-MS	cryogenic	2013	[240]

		honey blend							
125	Wines and coffee	Identification of potent odorants in Shiraz wine and the headspace of ground coffee	HS-SPME	qualitative/ untargeted	MSL	FID, qMS	LMCS	2015	[128]
126	Yerba mate	Analysis of the volatile fraction of yerba mate	HS-SPME	qualitative/ untargeted	MSL	qMS	thermal, non-moving quad-jet dual stage	2009	[241]
127	Artichoke (*Cynara scolymus* L.)	Understanding of the volatile composition of artichoke	LLE	qualitative/ untargeted	MSL	qMS	thermal, non-moving quad-jet dual stage	2014	[142]
128	Plants	Analysis of plant and insect emitted volatile components	HS-SPME	qualitative/ untargeted	MSL	qMS	thermal	2012	[242]
129	Malaysian soursop	Analysis of Malaysian soursop (*Annona muricata*) volatile flavor compounds	HS-SPME	qualitative/ untargeted	MSL	TOF-MS	thermal	2011	[22]
130	Barley	Analysis of volatile compounds of roasted barley	HS-SPME	qualitative/ untargeted	MSL	TOF-MS	thermal, non-moving quad-jet	2007	[20]

							dual stage		
131	Cress	Identification of odorant trace constituents in Indian cress (Tropaeolum majus L.)	HS-SPME	qaulitative/ untargeted	MSL	TOF-MS	cryogenic	2010	[243]
132	Oils	Analysis of volatile compounds of Neroli oil	HS-SPME	qualitative/ targeted	MSL	TOF-MS	thermal	2012	[244]
133	Cacao beans	Analyzis of volatile compounds from cacao beans	HS-SPME	quantitative/ targeted	MSL	TOF-MS	thermal	2009	[245]
134	Artemisia annua L.	Analyzis of the volatile oil of Artemisia annua L.	HS-SPME	qualitative/ untargeted	MSL, PCA	TOF-MS	thermal, non-moving quad-jet dual stage	2007	[175]
135	Wines	Quantitative determination of volatile compounds of Chardonnay wines	HS-SPME	quantitative/ targeted	MSL, OPLS-DA	TOF-MS	thermal, non-moving quad-jet dual stage	2014	[135]
136	Hazelnuts and Gianduja pastes	Quantitative fingerprinting of volatiles in roasted hazelnuts and in Gianduja pastes	HS-SPME	quantitatie/ targeted	MSL	qMS	thermal	2013	[246]

137	Wines and coffee	Identification of potent odourants in wine and brewed coffee	SPE	quantitative/ targeted	MSL	TOF-MS, FID, FPD	LMCS	2011	[127]
138	Shrimps	Investigation the aroma of cooked shrimps	HS-SPME	qualitative/ untargeted	MSL	TOF-MS	cryogenic	2009	[247]
139	Chocolate	Analysis of volatiles compounds from chocolate samples	HS-SPME	qualitative/ untargeted	MSL	qMS	cryogenic	2014	[248]
140	Oils	Characterization of oil from the pyrolysis of sugar cane straw and its fractions	PLE	qualitative/ untargeted	MSL, KI	qMS	thermal	2013	[249]
141	Essentials oils	Analysis of the chemical composition of the essential oil of Polygonum minus Huds.	PLE	qualitative/ targeted	MSL	TOF-MS	thermal	2010	[250]
142	Dairy spread extract and dairy and non-dairy sour cream	Analysis of flavour compounds in dairy spread extract and dairy and non-dairy sour cream samples	SAFE, CFD	qualitative/ untargeted	MSL	TOF-MS	LMCS	2003	[251]

143	Coffee beans	Analysis of roasted coffee bean volatiles	HS-SPME	semi-quantitative/ targeted	MSL	TOF-MS, FID	LMCS	2004	[122]
144	Bergamot essential oils	Fast chiral analysis of bergamot essential oils	HS-SPME	qualitative/ untargeted	MSL	qMS	thermal	2002	[156]
145	Chinese liquors	Characterization of the volatile compounds in Chinese liquors	HS-SPME	qualitative/ untargeted	MSL	TOF-MS	cryogenic	2007	[121]
146	Herbs	Aroma analyzis of 9 herbs	HS-SPME	qualitative/ untargeted	MSL	TOF-MS	cryogenic	2012	[171]
METHOD OPTIMIZATION									
147	Essential oils from rosemary and oregano	The optimization of the GC × GC set-up to make possible the analysis of essential oils from rosemary and oregano	HS-SPME	quantitative/ targeted	MSL	FID/qMS	valve	2012	[48]
148	Apples	Define capabilities and limitations of SPME in apples samples	HS-SPME	qualitative/ untargeted	MSL, KI	TOF-MS	cryogenic	2013	[252]

149	Pastas, rices, sugars	Optimization of a comprehensive two-dimensional gas chromatography method, for the identification and quantification of mineral-oil contaminants	SPE	quantitative/ targeted	MSL	FID/qMS	cryogenic	2013	[140]
150	Honeys	Optimalization of the SPME method for the analysis of honey volatiles	HS-SPME	qualitative/ untargeted	MSL	TOF-MS	cryogenic	2007	[78]

MSL - confirmation with mass spectral library; KI - confirmation with Kovats indices; SAFE - solvent assisted flavour extraction; PLE - pressurized liquid extraction; CFD - critical fluid distillation; LMCS - longitudinally modulated cryogenic system; ASE- accelerated solvent extraction, GPC - gel permeation chromatography HVD- high vacuum distillation; LLE - liquid-liquid extraction; DLLME - dispersive liquid–liquid micro-extraction; PLE - Pressurized Liquid Extraction; QuEChERS - '*Quick, Easy, Cheap, Effective, Rugged, and Safe*' method; MSPD - matrix solid phase dispersion; DSPE - dispersive solid phase extraction; SBSE- stir bar sorptive extraction; SAFE- solvent assisted flavor evaporation; SPE - solid phase extraction; HS-SPME - headspace solid phase microextraction