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# Gas Chromatography in Food Authentication

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## Abstract

Authentication of food products and food fraud detection are of great importance in the modern society. The application of sophisticated instrumentation, such as gas chromatography (GC), with this aim helps to improve the protection of consumers. Gas chromatography mostly combined with the most powerful detector, a mass spectrometer (MS), and various multivariate data processing tools is in the last few decades being increasingly applied in authenticity and traceability of a wide spectra of food products. These include animal and plant products, beverages and honey. This chapter gives an overview of the most recent applications of gas chromatography technique in determining food authenticity, described in scientific literature.

**Keywords:** food products, authenticity, food fraud, consumer protection, gas chromatography

## 1. Introduction

The adulteration practices on food product market are known since ancient times [1, 2]. It was found that, during the nineteenth century, gypsum and alum were added to bakery flour to increase weight, strychnine was added to beer to increase bitterness, and salts of copper, lead, and mercury were added to sweets in order to get a beautiful color and gloss [3–5]. Consumer interest in safety, authenticity and quality of food products is constantly increasing [6]. Authenticity is related to truthfulness, so a food product can be said to be authentic if it was not subject to any fraud [7]. European and global food policies require food on the market to be authentic. This means that the label on the product must match its actual composition, origin (geographical, botanical and genetic) and the process of production (conventional, organic and traditional) [2, 8, 9]. With globalization, market development and rapid distribution systems, as well as expanding the range of food items, counterfeiting and contamination of food products, are becoming international in character, and the possible consequences are far-reaching [2, 4, 9–11]. The most common type of adulteration—economically motivated food adulteration—is defined as *a misleading and deliberate substitution or addition of certain ingredients to a food product in order to increase the apparent value of the product or reduce the cost of its production, with the consequence of a certain economic gain* [4, 5]. Depending on the nature of an added substituent, the obtained adulterated products may pose a potential danger to the health of the consumer. In this way, the determination of authenticity in the food industry is gaining health and safety aspects, in addition to the economic one [6, 8, 12]. With all this in mind, global

policies require strict monitoring and quality control of food. Therefore, there is a clear tendency toward the development of new techniques and analytical methods that would enable this goal to be achieved. Traditional and standard methods of analysis are still very commonly used. Due to lower costs and/or faster analytical protocols, there is an urge for new authentication methodologies that would be complementary or even replace existing ones [8, 9]. This trend is stimulated by consumers, regulatory bodies and the food industry itself. Contemporary authentication analysis is based on the detection and measurement of various chemical parameters that would have the potential of discrimination factors of the investigated food samples [2, 9]. According to Danezis et al. [2], the first 10 countries in the world that are most intensively engaged with food authentication, in addition to the United States and China, are members of the European Union. These countries actively subsidize and encourage the development of this scientific area [2]. The European Commission regulations and directives testify about the rights of consumers to get the genuine information about food products that they buy [13–15]. These regulations aim to prevent (i) fraud and misleading actions, (ii) adulteration of food products and (iii) any other fraudulent procedures. An example of a very frequent way of food adulteration is the substitution of some ingredient in a food item with a similar and cheaper one, so that the consumer cannot recognize this procedure [1, 6, 8, 16]. According to the literature data, food products mostly subjected to adulterations include cereal and bakery products, edible oils and fats, milk and dairy products, meat and fish, fruit and fruit juices, honey, coffee, tea, wine, organic products and many others [9, 11]. Basically, there are three analytical approaches to determine the authenticity of food products: (i) chemical approach, determination of the composition and content of various chemical components in food; (ii) biomolecular approach, analysis of DNA and proteins; and (iii) isotopic approach, determination of the composition of stable isotopes of certain atoms [7]. Chromatographic techniques are the most common choice in the analysis of the authenticity of most food items [2, 9]. This is partly because techniques, such as chromatography, can be applied both for the purpose of detecting adulterations and for the purpose of determining authenticity [7]. In addition, the analytical capability of mass spectrometry, often used in conjunction with chromatographic techniques, allows the characterization of a wide range of components in very complex systems [17]. Some authors believe that the future of determining food authenticity is reflected in the synergistic fusion of various complementary instrumental techniques and the processing of such a complex block of enormous amounts of data using modern techniques of multivariate analysis [6]. Since 2001, a large number of scientific articles have appeared, relating to food authentication using new or existing analytical techniques in combination with multivariate data analysis. However, it has to be noted that the adulteration practices are also very contemporary and in constant development, with constant interest in surpassing the power of the established analytical methods of their discovery [14].

This chapter represents a thorough overview of the analytical methods employing a GC technique that are dealing with authentication and adulteration detection of various types of foodstuffs. The methods described are published in scientific literature in the last two decades.

## **2. Authentication and adulteration detection in various food products**

### **2.1 Olive oil and other edible vegetable oils**

Edible vegetable oils represent a matrix which is usually analyzed with the application of GC. That is why there are a large number of papers dealing with

authentication and adulteration detection in this type of food, using GC. Among them, extra virgin and virgin olive oils are definitely the most investigated. The suggested analytical methods are focused on the determination of constituents in oil mixtures of high prices and quality, the discrimination of extra virgin olive oils from defected oils, the possibilities of the authentication of various edible oils and fats and the determination of geographical origin. Triacylglycerol composition, fatty acid composition,  $^{13}\text{C}/^{12}\text{C}$  and  $^2\text{H}/^1\text{H}$  ratios and enantiomeric distributions of certain compounds, and just in some cases volatile organics and phenolic compounds, are usually considered as discrimination factors. Considering that this kind of analysis provides a large amount of data, the recently published papers are almost exclusively coupling GC with various unsupervised and supervised techniques of multivariate chemometric data analysis. Among unsupervised principal component analysis is definitely the mostly used, and among supervised techniques and machine learning algorithms, there are many different described: LDA and SLDA, PLS-DA, OPLS-DA, SIMCA, ANN-MLP, R-SVM and OC-SVM and some other. **Table 1** lists chronological literature data on authentication and adulteration detection procedures of the most commonly investigated olive oil, and also edible oils of other plant species, and some examples of animal fats.

## 2.2 Honey and other bee products

The authenticity of honey and other bee products has two aspects. Authenticity in respect of production, i.e., to prevent adulteration by the addition of other food ingredients (various types of sugar syrups), and authenticity of botanical and geographical origin. The GC method for determining the addition of sugar syrups relies on carbohydrate profiling in combination with classical statistical procedures for data processing. However, methods for authentication of geographical and botanical origin of honey samples usually employ more complex sample preparations, such as solid-phase microextraction in a headspace mode, and more sophisticated instrumentation, such as multidimensional GC. These methods mostly rely on the analysis of volatile organic compounds and also usually involve the application of multivariate chemometric tools for data analysis—unsupervised and supervised pattern recognition techniques. Unsupervised techniques, PCA and HCA, are more commonly used, but some studies also report the application of supervised tools: LDA and SLDA, OPLS-DA, SIMCA and ANN-MLP. **Table 2** lists examples from literature data on authentication and adulteration detection procedures of honey and other bee products, such as beeswax, propolis and royal jelly.

## 2.3 Milk and dairy products

Authenticity of milk and dairy products, such as cheese and fermented milk, using GC, is usually based on the determination of fat content of samples: triacylglycerols and fatty acids. Therefore, it is usually enough to combine GC with FID, to perform a successful analysis. In some particular cases, MS or olfactometry is used (if the analytical method is based on determining volatile profiles of the samples). Methods described in the literature rarely use chemometric data analysis, in some cases PCA, LDA and PLS-DA, but rather rely on the application of classical statistics. Papers describing the authentication of milk and dairy products usually deal with discriminating organic from conventionally produced ones, discriminating samples according to geographical origin and according to the animal breed they are produced of. **Table 3** shows literature examples of authentication and adulteration detection practices in milk and dairy products, such as cheese.

Purpose of the study	Analytical technique	Chemometric technique	Ref.
<b>Olive oil</b>			
Discrimination of “Ligurian” from “non-Ligurian” olive oils	HS-SPME/GC-ITMS	LDA, ANN-MLP	[18]
Differentiation of monovarietal olive oils according to olive variety	HS-SPME/	PCA	[19]
	GC × GC-	PCA, HCA, PLS-	[20]
	TOF-MS	DA	[21]
	HT-GC-ITMS	—	[22]
Differentiation of extra virgin and virgin olive oils according to geographical origin (various regions in Spain, Italy)	HS-SPME/GC-MS	SLDA	[23]
	HS-SPME/GC-MS	—	[21]
	GC-C/P-IRMS	—	[24]
Discrimination of extra virgin olive oils from defected oils	HS-SPME/ GC × GC-MS	PCA, PLS-DA	[25]
Detection of extra virgin olive oil, virgin olive oil and olive oil adulteration (with various types of edible oils)	LC-GC-ITMS	—	[26]
	LC-chiral-GC-ITMS	—	[27]
	PCA	[28]	
	GC-MS	—	[29]
	SPME/	SIMCA, kNN,	[30]
	GC × GC-MS	PLSR	[31]
	GC-MS	—	[32]
	SPME/GC-MS	PCA, PLS	[33]
	GC-FID	PCA, TFA,	[34]
	GC-MS	SIMCA, PLS OC-	
GC-MS	SVM		
<b>Other edible oils</b>			
Discrimination of various vegetable oils according to botanical origin (sunflower, corn, sesame, soybean, olive, rapeseed, camellia, peanut, canola, palm, rice bran, coconut, grapeseed, hazelnut, walnut, apricot seed, red pepper seed, prikachberry, pumpkin)	GC-C-IRMS	CDA	[35]
	GC-C-IRMS	—	[36]
	HT-GC-FID	PCA	[37]
	GC-FID	PCA, KNN, CNN	[38]
	GC-FID	PCA, PLS	[32]
	HT-GC-MS	SIMCA, PLS,	[39]
	GC-MS	GA-PLS	[40]
	GC-MS	PCA, PLS-DA,	[41]
	GC-MS	OPLS-DA	[42]
	GC-MS	PCA, HCA, RF	[43]
	GC-MS	LDA, GA-SVM	
Differentiation of almond oils according to almond variety	HS-SPME/GC-MS	SLDA	[44]
Detection of corn oil adulteration	GC-C-IRMS	—	[45]
Detection of flaxseed oil adulteration	GC-MS	PCA, R-SVM	[46]
Detection of sesame oil adulteration	GC-FID	—	[47]
	GC-FID	SVM	[48]
	GC-MS	OC-SVM	[49]
Authenticity and geographical origin of pumpkin seed oil	GC-FID GC-C-IRMS	PCA, RDA	[50]
<b>Fats</b>			
Authenticity of cocoa butter	LC-GC-MS	—	[51]
Discrimination of various edible oils and fats (pig, mutton, beef and chicken)	GC-MS	PCA, PLS-DA, OPLS-DA	[40]

**Table 1.** Literature examples of authentication and adulteration detection procedures of olive oil and other edible oils and fats.

Purpose of the study	Analytical technique	Chemometric technique	Ref.
<b>Honey</b>			
Detection of the addition of sugar syrups to honey (high-fructose corn syrup and inverted syrup)	GC-FID	PCA	[52]
	GC-FID/MS	—	[53]
	GC-FID	—	[54]
Differentiation of four types of multifloral Portuguese honeys (produced in Madeira Island)	HS-SPME/GC-MS	PCA, SLDA	[55]
Authenticity of “Corsica” honey	HS-SPME/ GC × GC-TOF- MS	PCA, ANN- MPL LDA, SIMCA, SVM, DPLS	[56]
	HS-SPME/ GC × GC- TOF-MS		[57]
Detection of honey adulteration with high-fructose inulin syrups	GC-MS	—	[58]
Authenticity of thistle honey	HD-SPME/GC-MS	—	[59]
Authenticity of botanical origin of unifloral chestnut ( <i>Castanea sativa</i> L.) and eucalyptus ( <i>Eucalyptus globulus</i> Labill.) honeys	GC-MS	—	[60]
Differentiation between lemon blossom honey ( <i>Citrus limon</i> ) and orange blossom honey ( <i>Citrus</i> spp.)	GC-MS	PCA	[61]
Geographical origin identification of honey (samples from various regions of Greece; samples from various Mediterranean countries: Egypt, Greece, Morocco, Spain)	HS-GC-MS	—	[62]
	HS-SPME/GC-MS	HCA, SLDA,	[63]
	HS-GC-MS	kNN	[64]
	HS-SPME/GC- Q-TOF-MS	OPLS-DA,	[65]
	HS-SPME/GC-MS	SIMCA, OPLS-	[66]
	SPME-GC/MS	HCA PCA LDA LDA	[67]
Differentiation of honeys according to botanical origin: heather, raspberry, rape, alder buckthorn, lime, rosemary, chestnut, sunflower, acacia, thyme, orange, linden, amaranth, honeydew, citrus, <i>Gossypium</i> , rhododendron, alfalfa, white clover, carob, calden	HS-GC-MS	—	[62]
	SPME/GC-MS	LDA	[68]
	HS-GC-MS	OPLS-DA,	[64]
	SPME/chiral- GC × GC-MS	SIMCA, OPLS-	[69]
	SPME/GC-MS/O	HCA	[70]
	SPME-GC/MS	— AHC, CA PCA, HCA	[71]
Establishment of orange honey authenticity	SPME/GC-MS	—	[72]
<b>Other bee products</b>			
Authenticity of royal jelly; detection of the addition of sugar syrups	HR-GC	—	[73]
Characterization of traditional plant syrups from Spain, namely, palm honey (miel de palma), must syrup (arrope) and sugarcane honey (miel de caña)	GC-MS	—	[74]
Detection of adulterated beeswax from <i>Apis mellifera</i> L.	HT-GC-FID/MS	—	[75]
	HT-GC-FID/MS	HCA, PCA, LDA	[76]
Geographical origin identification of propolis	HS/GC-MS/O	PCA	[77]
Establishment of sugarcane honey authenticity	HS-SPME/GC-MS	PCA, LDA	[78]

**Table 2.**  
 Literature examples of authentication and adulteration detection procedures of honey and other bee products.

Purpose of the study	Analytical technique	Chemometric technique	Ref.
<b>Milk</b>			
Authenticity of goat milk	GC-FID	—	[79]
Differentiation between cow milk produced in the lowlands, mountains and highlands of Switzerland	HR-GC-FID	—	[80]
Authenticity of milk fat: detection of foreign fat in milk fat (such as pork lard, bovine tallow, fish oil, peanut oil, corn oil, olive oil, soy oil, sunflower oil, coconut fat)	GC-FID	—	[81]
	UFM-GC-FID	—	[82]
	FID	LDA	[83]
	GC-FID	—	[84]
	GC-FID	—	[85]
Differentiation of milk produced under conventional and organic management	GC-FID	—	[86]
	GC-FID	—	[87]
	GC-MS	—	[88]
Differentiation of cow, goat, sheep, water buffalo, donkey, horse and camel milk	GC-FID	PCA	[89]
Determining the origin of milk samples: hay milk vs. conventional (silage) milk	GC-FID	PCA, PLS-DA	[90]
<b>Dairy products</b>			
Geographic origin of Emmental cheese	GC-FID	—	[91]
	HS-GC-FID/MS	PCA	[92]
Differentiation of Grana Padano, Parmigiano-Reggiano and Grana Trentino cheeses	GC-O	PCA	[93]
Examining foreign fat origin in cheese from cow milk fat	GC-FID	—	[94]
Differentiation between certified organic and conventional probiotic fermented milks	GC-FID	—	[95]
Quality control for Parmigiano-Reggiano cheese	GC-MS	PCA	[96]

**Table 3.**  
*Literature examples of authentication and adulteration detection procedures of milk and various dairy products.*

## 2.4 Fruits and fruit-made beverages

Most of the papers dealing with fruit authenticity testing using GC are focused on determining discriminating factors that will enable discrimination of varieties of certain fruit species. These factors are mostly constituted of free and bound volatile compounds belonging to different chemical groups, namely, linear and branched esters, terpenes, alcohols and others. The paper published by Kurz et al. [97] is an exception, which is dealing with the analysis of neutral sugars of cell wall polysaccharide profiles of apricots, peaches and pumpkins using GC-FID. In some cases GC was also combined with other analytical techniques, thus enabling the wider spectra of chemical species to be included in the analysis, such as LC, in order to include nonvolatile carbohydrates, fatty acids and organic acids. The obtained data were mainly processed using multivariate data analysis techniques, such as HCA, PCA, PLS-DA, LDA and OPLS-DA. Older investigations usually do not include multivariate data analysis. Schmarr and Bernhardt [98] used image processing techniques in order to process the data obtained after comprehensive two-dimensional GC

Purpose of the study	Analytical technique	Chemometric technique	Ref.
<b>Fruits</b>			
Differentiation of blackcurrant ( <i>Ribes nigrum</i> L.) berries	SPME/GC-FID	—	[97]
Differentiation of apricots ( <i>Prunus armeniaca</i> L.), peaches ( <i>Prunus persica</i> L.) and pumpkins ( <i>Cucurbita</i> sp.)	GC-FID	—	[99]
Differentiation between <i>Passiflora</i> fruit species	HS-SPME/GC-MS	PCA	[100]
Discrimination of red grape varieties of southern Italy (Aglanico, Uva di Troia, Negroamaro, Primitivo)	GC-MS	PCA	[101]
Differentiation of apples, pears and quince fruit	HS-SPME/ GC × GC	—	[98]
Classification of apple varieties (Golden Delicious, Granny Smith, Pinova and Stark Delicious)	HS-SPME/GC- TOF-MS	PCA, PLS-DA	[102]
Differentiation between grape varieties: <i>Vitis vinifera</i> , <i>Vitis cinerea</i> and interspecific crosses	GC-MS	HCA	[103]
Differentiation of Chinese bayberry cultivars ( <i>Myrica rubra</i> )	HS-SPME/GC-MS HS-SPME/GC- MS/O	PCA —	[104] [105]
Discrimination of nine passion fruits: yellow, purple, lemon, orange, pineapple, peach, melon, banana and tomato	HS-SPME/GC-MS	PCA, PLS-DA	[106]
Differentiation between Tanzanian grown fruits: mango, pineapple, jackfruit, baobab and tamarind	GC-MS	HCA, PCA	[107]
Discrimination of <i>Eugenia uniflora</i> L. biotypes	HS-SPME/GC-MS	PCA, HCA	[108]
Differentiation between date palm fruit ( <i>Phoenix dactylifera</i> L.) varieties from Egypt	SPME/GC-MS	PCA, HCA, OPLS-DA	[109]
Characterization of organic oranges ( <i>Citrus sinensis</i> L. Osbeck)	HS-SPM/GC-MS	PLS-DA	[110]
Differentiation of sun-dried raisins made from different grape varieties	HS-SPME/GC- TOF-MS	—	[111]
Differentiation between citrus species: mandarin, sweet orange, sour orange, papeda, pummelo, lemon, <i>Fortunella Swingle</i>	GC-MS	HCA	[112]
Differentiation of apple cultivars from geographical origin and growing conditions (organic and conventional)	HS-SPME/GC-MS	PLS-DA	[113]
Differentiation of Chinese Jujube varieties	HS-SPME/GC-MS	HCA	[114]
<b>Fruit beverages</b>			
Detecting adulteration of blackcurrant juice	GC-FID	—	[115]
Authentication of apple and orange juice	GC-FID	—	[116]
Detecting the addition of aromas to fruit beverages	SPME/chiral-GC- MS	—	[117]
Citrus juice classification (lemon, grapefruit, mandarin, orange, lime)	HS-SPME/GC-MS	LDA	[118]
Assessment of premium organic orange juices authenticity	HS-SPME/GC-MS	PLS-DA	[119]

**Table 4.**  
 Literature examples of authentication and adulteration detection procedures of various fruits and fruit juices.

analysis. **Table 4** chronologically lists some literature examples on authentication and adulteration procedures of various fruit species and fruit-made juices.

## 2.5 Cereals and bakery products

Cereals, pseudocereals, flours and bread, as mostly used bakery products in human nutrition, are usually differentiated according to varietal, botanical or geographical origin by combining GC analysis with chemometric processing of the obtained data. The chemical compounds that have the role of discriminating factors usually involve small molecules, such as simple soluble sugars and free fatty acids. Chemometric methods involve most often exploratory data analysis techniques, such as PCA, PCO and HCA, but in some cases also classification methods of LDA and QDA were applied to measure the classification and prediction abilities. **Table 5** chronologically lists some literature examples of authentication and adulteration detection practices of cereals, flour and the most commonly used bakery product in human nutrition-bread.

## 2.6 Meat, fish and seafood

The studies of authenticity of seafood and meat products using a GC technique usually focus on the determination of freshness of a seafood or meat product. Chemometric techniques, such as PCA, were able to successfully discriminate between fresh samples, deteriorated samples and gradually decaying samples of seafood, and ANN were employed in order to classify samples of fresh meat, frozen-thawed meat and spoiled meat. The PCA of gas chemometric fingerprints was able to show separation not only between oyster species but also between oysters originating from different cultivation areas, as well as oysters harvested at

Purpose of the study	Analytical technique	Chemometric technique	Ref.
<b>Cereals</b>			
Differentiation between <i>Triticum durum</i> and <i>Triticum aestivum</i>	GC-FID	PCA, LDA, QDA	[120]
Differentiation between hexaploid ( <i>T. aestivum</i> , <i>T. spelta</i> ) and tetraploid ( <i>T. durum</i> , <i>T. dicoccon</i> ) wheats	GC-MS	—	[121]
Classifications of cereals (wheat and corn) used in DDGS material by geographical and botanical origin	GC-FID	PLS-DA	[122]
<b>Flour</b>			
Differentiation of corn and small grain flour (wheat, rye, triticale, barley, oats)	GC-MS	HCA, PCO HCA, PCA	[123] [124]
Differentiation of corn and oat flour, from other small grains (wheat, barley, triticale, rye)	GC-MS	HCA, PCO	[125]
Differentiation of flours of corn, spelt, buckwheat, amaranth and small grains (wheat, rye, triticale, oats, barley)	GC-MS	HCA, PCA	[126]
<b>Bakery products</b>			
The content of buckwheat flour in wheat bread	GC-MS	HCA HCA, PCA	[127] [128]

**Table 5.** Literature examples of authentication and adulteration detection procedures of cereals, flour and bakery products.

different time intervals. There was only one paper found in the literature that deals with differentiation of meat according to the breed origin. The PCA was successfully applied to discriminate between samples of pork, chicken, beef and mutton meat. **Table 6** represents a chronological list of examples of authentication and adulteration detection procedures of various types of meat, fish and seafood.

Purpose of the study	Analytical technique	Chemometric technique	Ref.
<b>Fish and seafood</b>			
Differentiation between fresh and deteriorated oyster <i>Crassostrea gigas</i>	HS-SPME/GC-MS	PCA	[129]
Differentiation between fresh and frozen-thawed cultured gilthead sea bream fish ( <i>Sparus aurata</i> )	SPME/GC-MS	—	[130]
Razor clam ( <i>Sinonovacula constricta</i> Lamarck), redspot swimming crab ( <i>Portunus sanguinolentus</i> Herbst) and prawn ( <i>Penaeus japonicus</i> (Bate; Kuruma prawn)) freshness determination	HS-SPME/GC-MS	PCA	[131]
Differentiation of European flat oyster ( <i>Ostrea edulis</i> ) and Pacific cupped oyster ( <i>Crassostrea gigas</i> ): species, different cultivation areas, different time intervals of harvest	GC-FID GC-MS	PCA	[132]
<b>Meat</b>			
Halal authentication of pork meat	HS/GC-MS	PCA	[133]
Differentiation of fresh and frozen pork	UFGC	PCA, ANN	[134]

**Table 6.**  
 Literature examples of authentication and adulteration detection procedures of meat products and seafood.

Purpose of the study	Analytical technique	Chemometric technique	Ref.
<b>Coffee</b>			
Differentiation between arabica ( <i>Coffea arabica</i> Linn.) and robusta ( <i>Coffea canephora</i> Pierre ex Froehner var. <i>robusta</i> ) coffees, either in green or in roasted stage	HR-GC-FID	HCA, CVA, DA	[135]
Determining the geographical origin of coffee samples	HS-SPME/GC-TOF-MS	PCA	[136]
<b>Tea</b>			
Differentiation of <i>Echinacea</i> species ( <i>E. angustifolia</i> , <i>E. pallida</i> , <i>E. purpurea</i> )	GC-MS	HCA, PCA, LDA	[137]
Discrimination of oolong tea ( <i>Camellia sinensis</i> ) varieties	HS-SPME/GC-MS	PCA, HCA, SLDA	[138]
Discrimination of two roselle ( <i>Hibiscus sabdariffa</i> ) flower cultivars	SPME/GC-MS	PCA, HCA, OPLS-DA	[139]
Discrimination of different teas ( <i>Camellia sinensis</i> )	HS-SPME/chiral-GC-MS	HCA, PLS-DA	[140]
Discrimination of American ginseng ( <i>Panax quinquefolius</i> L.) and Asian ginseng ( <i>Panax ginseng</i> Meyer)	GC-MS	PCA, PLS	[141]

**Table 7.**  
 Literature examples of authentication and adulteration detection procedures of coffee and tea.

## 2.7 Coffee and tea

Differentiation of coffee samples is based mostly on fatty acid profiles and volatile and semi-volatile compounds (organic acids, sugars, terpenoids). Differentiations of various tea plants were based exclusively on volatile components. In order to enable differentiations and classifications of investigated samples of beverages, the data obtained after GC analysis were combined with various chemometric techniques: HCA, PCA, SLDA and OPLS-DA. **Table 7** represents chronological literature data on the authentication and adulteration detection procedures of coffee and tea from various plant species.

## 3. Conclusions

Gas chromatograph, as a common instrument in most analytical laboratories worldwide, can be successfully applied in authentication and fraud detection procedures of various food and beverage products, such as olive oil and other edible vegetable oils, honey and other bee products, milk and dairy products, cereals and bakery products, meat, fish and seafood, as well as coffee and tea. In this manner, gas chromatograph is coupled to flame ionization detector or single/tandem mass spectrometers. It can be concluded that utilization of a GC device in further development of authentication methodologies could provide us with meaningful results, thus representing a significant contribution to this emerging field in the future.

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## Conflict of interest

The authors declare that they have no conflict of interest.

## Acronyms and abbreviations

AHC	agglomerative hierarchical clustering
ANN	artificial neural networks
C-IRMS	combustion isotope ratio mass spectrometry
CA	correspondence analysis
CDA	canonical discriminant analysis
CNN	counterpropagation neural network
CVA	canonical variates analysis
DA	discriminant analysis
DPLS	discriminant partial least squares
FID	flame ionization detector
GA	genetic algorithm
GC	gas chromatography
GC-chiral GC	fast multiple heart-cut enantioselective multidimensional gas chromatography

chiral GC × GC	enantioselective comprehensive two-dimensional gas chromatography
HCA	hierarchical cluster analysis
HR	high resolution
HS	headspace
HT	high temperature
IR	isotope ratio
IT	ion-trap
kNN	k-nearest neighbors
KNN	Kohonen neural network
LC	liquid chromatography
LDA	linear discriminant analysis
MLP	multilayer perceptron
MCOCPLS	Monte Carlo one-class partial least squares
MS	mass spectrometry
O	olfactometry
OC-SVM	one-class support vector machine
OPLS-DA	orthogonal projections to latent structures discriminant analysis
P-IRMS	pyrolysis isotope ratio mass spectrometry
PCA	principal component analysis
PCoA	principal coordinate analysis
PLS	principal least squares regression
Q-TOF-MS	quadrupole accurate mass time-of-flight mass spectrometry
QDA	quadratic discriminant analysis
R-SVM	recursive support vector machine
RDA	regularized discriminant analysis
RF	random forests
SIMCA	soft independent modeling of class analogy
SLDA	stepwise linear discriminant analysis
SPME	solid-phase microextraction
SVM	support vector machine
TOF	time-of-flight
UF	ultrafast module

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## References

- [1] Oliveri P, Downey G. Multivariate class modeling for the verification of food-authenticity claims. *Trends in Analytical Chemistry*. 2012;**35**:74-86
- [2] Danezis GP, Tsagkaris AS, Camin F, Brusic V, Georgiou CA. Food authentication: Techniques, trends & emerging approaches. *Trends in Analytical Chemistry*. 2016a;**85**:123-132
- [3] Accum F. *A Treatise on Adulterations of Food and Culinary Poisons*. London, UK: Longman; 1820
- [4] Manning L, Soon JM. Developing systems to control food adulteration. *Food Policy*. 2014;**49**:23-32
- [5] Spink J, Moyer DC. Defining the public health threat of food fraud. *Journal of Food Science*. 2011;**76**:157-163
- [6] Borrás E, Ferré J, Boque R, Mestres M, Acena L, Bustó O. Data fusion methodologies for food and beverage authentication and quality assessment—A review. *Analytica Chimica Acta*. 2015;**891**:1-14
- [7] Cuadros-Rodríguez L, Ruiz-Samblas C, Valverde-Som L, Perez-Castano E, Gonzalez-Casado A. Chromatographic fingerprinting: An innovative approach for food 'identification' and food authentication—A tutorial. *Analytica Chimica Acta*. 2016;**909**:9-23
- [8] Cubero-Leon E, Peñalver R, Maquet A. Review on metabolomics for food authentication. *Foodservice Research International*. 2014;**60**:95-107
- [9] Danezis GP, Tsagkaris AS, Brusic V, Georgiou CA. Food authentication: State of the art and prospects. *Current Opinion in Food Science*. 2016b;**10**:22-31
- [10] WDS. Metabolomics: Applications to food science and nutrition research. *Trends in Food Science and Technology*. 2008;**19**:482-493
- [11] Moore JC, Spink J, Development LM. Application of a database of food ingredient fraud and economically motivated adulteration from 1980 to 2010. *Journal of Food Science*. 2012;**77**:118-126
- [12] Manning L. Food fraud: Policy and food chain. *Current Opinion in Food Science*. 2016;**10**:16-21
- [13] European Commission Regulation (EC) No 178/2002 of the European Parliament and of the council of 28 January 2002 laying down the general principles and requirements of food law, establishing the European Food Safety Authority and laying down procedures in matters of food safety. *Official Journal of the European Communities*. 2002;**L31**:1-24
- [14] Reid LM, O'Donnell CP, Downey G. Recent technological advances for the determination of food authenticity. *Trends in Food Science and Technology*. 2006;**17**:344-353
- [15] European Commission Regulation (EU) No 1169/2011 of the European Parliament and of the council of 25 October 2011 on the provision of food information to consumers. *Official Journal of the European Communities*. 2011;**L304**(/18):18-62
- [16] Corrado G. Advances in DNA typing in the agro-food supply chain. *Trends in Food Science and Technology*. 2016;**52**:80-89
- [17] Gallo M, Ferranti P. The evolution of analytical chemistry methods in foodomics. *Journal of Chromatography A*. 2016;**1428**:3-15
- [18] Cajka T, Riddelova K, Klimankova E, Cerna M, Pudil F,

- Hajslova J. Traceability of olive oil based on volatiles pattern and multivariate analysis. *Food Chemistry*. 2010;**121**: 282-289
- [19] Torres Vaz-Freire L, Gomes da Silva MDR, Costa Freitas AM. Comprehensive two-dimensional gas chromatography for fingerprint pattern recognition in olive oils produced by two different techniques in Portuguese olive varieties *Galega Vulgar*, *Cobranca*, *osa* e *Carrasquenha*. *Analytica Chimica Acta*. 2009;**633**:263-270
- [20] Ruiz-Samblás C, Cuadros-Rodríguez L, González-Casado A, de Paula Rodríguez García F, de la Mata-Espinosa P, Bosque-Sendra JM. Multivariate analysis of HT/GC-(IT)MS chromatographic profiles of triacylglycerol for classification of olive oil varieties. *Analytical and Bioanalytical Chemistry*. 2011;**399**:2093-2103
- [21] Cecchi T, Alfei B. Volatile profiles of Italian monovarietal extra virgin olive oils via HS-SPME-GC-MS: Newly identified compounds, flavors molecular markers, and terpenic profile. *Food Chemistry*. 2013;**141**:2025-2035
- [22] Bajoub A, Pacchiarotta T, Hurtado-Fernández E, Olmo-García L, García-Villalba R, Fernández-Gutiérrez A, et al. Comparing two metabolic profiling approaches (liquid chromatography and gas chromatography coupled to mass spectrometry) for extra-virgin olive oil phenolic compounds analysis: A botanical classification perspective. *Journal of Chromatography. A*. 2016;**1428**:267-279
- [23] Pizarro C, Rodriguez-Tecedor S, Perez-del-Notario N, Gonzalez-Saiz JM. Recognition of volatile compounds as markers in geographical discrimination of Spanish extra virgin olive oils by chemometric analysis of non-specific chromatography volatile profiles. *Journal of Chromatography. A*. 2011;**1218**:518-523
- [24] Paolini M, Bontempo L, Camina F. Compound-specific  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  analysis of olive oil fatty acids. *Talanta*. 2017;**174**:38-43
- [25] Purcaro G, Cordero C, Liberto E, Bicchi C, Contea LS. Toward a definition of blueprint of virgin olive oil by comprehensive two-dimensional gas chromatography. *Journal of Chromatography. A*. 2014;**1334**:101-111
- [26] Blanch GP, del Mar Caja M, del Castillo MLR, Herraiz M. Comparison of different methods for the evaluation of the authenticity of olive oil and hazelnut oil. *Journal of Agricultural and Food Chemistry*. 1998;**46**:3153-3157
- [27] del Castillo MLR, Herraiz M, Blanch GP. Determination of the enantiomeric composition of  $\gamma$ -lactones in edible oils by on-line coupled high performance liquid chromatography and gas chromatography. *Journal of Agricultural and Food Chemistry*. 2000;**48**:1186-1190
- [28] Dourtoglou VG, Dourtoglou T, Antonopoulos A, Stefanou E, Lalas S, Poulos C. Detection of olive oil adulteration using principal component analysis applied on total and Regio FA content. *JAOCS*. 2003;**80**:203-208
- [29] Flores G, del Castillo MLR, Blanch GP, Herraiz M. Detection of the adulteration of olive oils by solid phase microextraction and multidimensional gas chromatography. *Food Chemistry*. 2006;**97**:336-342
- [30] Priego Capote F, Ruiz Jiménez J, Luque de Castro MD. Sequential (step-by-step) detection, identification and quantitation of extra virgin olive oil adulteration by chemometric treatment of chromatographic profiles. *Analytical and Bioanalytical Chemistry*. 2007;**388**: 1859-1865
- [31] Sakouhi F, Absalon C, Flamini G, Cioni PL, Kallel H, Boukhchina S. Lipid

- components of olive oil from Tunisian cv. Sayali: Characterization and authenticity. *Comptes Rendus Biologies*. 2010;**333**:642-648
- [32] Rohman A, Che Man YB. Authentication of extra virgin olive oil from sesame oil using FTIR spectroscopy and gas chromatography. *International Journal of Food Properties*. 2011;**15**:1309-1318
- [33] Monfreda M, Gobbi L, Grippa A. Blends of olive oil and seeds oils: Characterisation and olive oil quantification using fatty acids composition and chemometric tools. *Food Chemistry*. 2014;**145**:584-592
- [34] Zhang L, Yuan Z, Li P, Wang X, Mao J, Zhang Q, et al. Targeted multivariate adulteration detection based on fatty acid profiles and Monte Carlo one-class partial least squares. *Chemometrics and Intelligent Laboratory Systems*. 2017;**169**:94-99
- [35] Kelly S, Parker I, Sharman M, Dennis J, Goodall I. Assessing the authenticity of single oils using fatty acid stable carbon ( $^{13}\text{C}/^{12}\text{C}$ ). *Food Chemistry*. 1997;**59**:181-186
- [36] Woodbury SE, Evershed RP, Rossell JB.  $\delta^{13}\text{C}$  analyses of vegetable oil fatty acid components, determined by gas chromatography-combustion-isotope ratio mass spectrometry, after saponification or regiospecific hydrolysis. *Journal of Chromatography A*. 1998;**805**:249-257
- [37] Park JR, Lee DS. Detection of adulteration in olive oils using triacylglycerols compositions by high temperature gas chromatography. *Bulletin of the Korean Chemical Society*. 2003;**24**:527-530
- [38] Brodnjak-Voncina D, Cencic Kodbab Z, Novic M. Multivariate data analysis in classification of vegetable oils characterized by the content of fatty acids. *Chemometrics and Intelligent Laboratory Systems*. 2005;**75**:31-43
- [39] Ruiz-Samblás C, Marini F, Cuadros-Rodríguez L, González-Casado A. Quantification of blending of olive oils and edible vegetable oils by triacylglycerol fingerprint gas chromatography and chemometric tools. *Journal of Chromatography B*. 2012;**910**:71-77
- [40] Fang G, Goh JY, Tay M, Lau HF, Li SFY. Characterization of oils and fats by  $^1\text{H}$  NMR and GC/MS fingerprinting: Classification, prediction and detection of adulteration. *Food Chemistry*. 2013;**138**:1461-1469
- [41] Zhang L, Li P, Sun X, Wang X, Xu B, Wang X, et al. Adulteration detection of vegetable oils based on fatty acid profiles. *Journal of Agricultural and Food Chemistry*. 2014;**62**:8745-8751
- [42] Troya F, Lerma-García MJ, Herrero-Martínez JM, Simó-Alfonso EF. Classification of vegetable oils according to their botanical origin using n-alkane profiles established by GC-MS. *Food Chemistry*. 2015;**167**:36-39
- [43] Li X, Kong W, Shi W, Shen Q. A combination of chemometrics methods and GC-MS for the classification of edible vegetable oils. *Chemometrics and Intelligent Laboratory Systems*. 2016;**155**:145-150
- [44] Beltrán A, Ramos M, Grané N, Martín ML, Garrigós MC. Monitoring the oxidation of almond oils by HS SPME-GC-MS and ATR-FTIR: Application of volatile compounds determination to cultivar authenticity. *Food Chemistry*. 2011;**126**:603-609
- [45] Woodbury SE, Evershed RP. Detection of vegetable oil adulteration using gas chromatography combustion/isotope ratio mass spectrometry. *Analytical Chemistry*. 1995;**67**:2685-2690

- [46] Sun X, Zhang L, Li P, Xu B, Ma F, Zhang Q, et al. Fatty acid profiles based adulteration detection for flaxseed oil by gas chromatography mass spectrometry. *LWT—Food Science and Technology*. 2015;**63**:430-436
- [47] Park YW, Chang P-S, Lee JH. Application of triacylglycerol and fatty acid analyses to discriminate blended sesame oil with soybean oil. *Food Chemistry*. 2010;**123**:377-383
- [48] Peng D, Bi Y, Ren X, Yang G, Sun S, Wang X. Detection and quantification of adulteration of sesame oils with vegetable oils using gas chromatography and multivariate data analysis. *Food Chemistry*. 2015;**188**:415-421
- [49] Zhang L, Huang X, Li P, Naf W, Jiang J, Mao J, et al. Multivariate adulteration detection for sesame oil. *Chemometrics and Intelligent Laboratory Systems*. 2017;**161**:147-150
- [50] Potocnik T, Ogrinc N, Potocnik D, Košir IJ. Fatty acid composition and  $\delta^{13}\text{C}$  isotopic ratio characterisation of pumpkin seed oil. *Journal of Food Composition and Analysis*. 2016;**53**: 85-90
- [51] Kamm W, Dionisi F, Fay L-B, Hischenhuber C, Schmarr H-G, Engel K-H. Analysis of steryl esters in cocoa butter by on-line liquid chromatography-gas chromatography. *Journal of Chromatography. A*. 2001;**918**:341-349
- [52] Cotte JF, Casabianca H, Chardon S, Lheritier J, Grenier-Loustalot MF. Application of carbohydrate analysis to verify honey authenticity. *Journal of Chromatography. A*. 2003;**1021**:145-155
- [53] Ruiz-Matute AI, Soria AC, Martinez-Castro I, Sanz ML. New methodology based on GC-MS to detect honey adulteration with commercial syrups. *Journal of Agricultural and Food Chemistry*. 2007;**55**:7264-7269
- [54] Kaškonienė V, Venskutonis P, Čeksterytė V. Sugar analysis for authenticity evaluation of honey in Lithuanian market. *Acta Alimentaria*. 2011;**40**:205
- [55] Pontes M, Marques JC, Camara JS. Screening of volatile composition from Portuguese multifloral honeys using headspace solid-phase microextraction-gas chromatography-quadrupole mass spectrometry. *Talanta*. 2007;**74**:91-103
- [56] Cajka T, Hajslova J, Pudil F, Ridelova K. Traceability of honey origin based on volatiles pattern processing by artificial neural networks. *Journal of Chromatography. A*. 2009;**1216**:1458-1462
- [57] Stanimirova I, Ustun B, Cajka T, Ridelova K, Hajslova J, Buydens LMC, et al. Tracing the geographical origin of honeys based on volatile compounds profiles assessment using pattern recognition techniques. *Food Chemistry*. 2010;**118**:171-176
- [58] Ruiz-Matute AI, Rodriguez-Sanchez S, Sanz ML, Martinez-Castro I. Detection of adulterations of honey with high fructose syrups from inulin by GC analysis. *Journal of Food Composition and Analysis*. 2010a;**23**:273-276
- [59] Bianchi F, Mangia A, Mattarozzi M, Musci M. Characterization of the volatile profile of thistle honey using headspace solid-phase microextraction and gas chromatography-mass spectrometry. *Food Chemistry*. 2011;**129**:1030-1036
- [60] Alissandrakis E, Tarantilis PA, Pappas C, Harizanis PC, Polissiou M. Investigation of organic extractives from unifloral chestnut (*Castanea sativa* L.) and eucalyptus (*Eucalyptus globulus* Labill.) honeys and flowers to identification of botanical marker compounds. *LWT- Food Science and Technology*. 2011;**44**:1042-1051

- [61] Escriche I, Kadar M, Juan-Borrás M, Domenech E. Using flavonoids, phenolic compounds and headspace volatile profile for botanical authentication of lemon and orange honeys. *Foodservice Research International*. 2011;**44**:1504-1513
- [62] Radovic BS, Careri M, Mangia A, Musci M, Gerboles M, Anklam E. Contribution of dynamic headspace GC-MS analysis of aroma compounds to authenticity testing of honey. *Food Chemistry*. 2001;**72**:511-520
- [63] Baroni MVN, Nores ML, Del Pilar Diáz M, Chiabrando GA, Fassano JB, Costa C, et al. Determination of volatile organic compound patterns characteristic of five unifloral honey by solid-phase microextraction-gas chromatography-mass spectrometry coupled to chemometrics. *Journal of Agricultural and Food Chemistry*. 2006;**54**:7235-7724
- [64] Aliferis KA, Tarantilis PA, Harizanis PC, Alissandrakis E. Botanical discrimination and classification of honey samples applying gas chromatography/mass spectrometry fingerprinting of headspace volatile compounds. *Food Chemistry*. 2010;**121**:856-862
- [65] Moniruzzaman M, Rodríguez I, Ramil M, Cela R, Sulaiman SA, Gan SH. Assessment of gas chromatography time-of-flight accurate mass spectrometry for identification of volatile and semi-volatile compounds in honey. *Talanta*. 2014;**129**:505-515
- [66] Karabagias IK, Badeka A, Kontakos S, Karabournioti S, Kontominas MG. Characterisation and classification of Greek pine honeys according to their geographical origin based on volatiles, physicochemical parameters and chemometrics. *Food Chemistry*. 2014;**146**:548-557
- [67] Karabagias IK, Louppis AP, Karabournioti S, Kontakos S, Papastephanou C, Kontominas MG. Characterization and geographical discrimination of commercial *Citrus* spp. honeys produced in different Mediterranean countries based on minerals, volatile compounds and physicochemical parameters, using chemometrics. *Food Chemistry*. 2017;**217**:445-455
- [68] Senyuva HZ, Gilbert J, Silici S, Charlton A, Dal C, Gurel N, et al. Profiling Turkish honeys to determine authenticity using physical and chemical characteristics. *Journal of Agricultural and Food Chemistry*. 2009;**57**:3911-3919
- [69] Španik I, Pazitna A, Šiška P, Szolcsanyi P. The determination of botanical origin of honeys based on enantiomer distribution of chiral volatile organic compounds. *Food Chemistry*. 2014;**158**:497-503
- [70] Seisonen S, Kivima E, Vene K. Characterisation of the aroma profiles of different honeys and corresponding flowers using solid-phase microextraction and gas chromatography-mass spectrometry/olfactometry. *Food Chemistry*. 2015;**169**:34-40
- [71] Tahir HE, Xiaobo Z, Xiaowei H, Jiyong S, Mariod AA. Discrimination of honeys using colorimetric sensor arrays, sensory analysis and gas chromatography techniques. *Food Chemistry*. 2016;**206**:37-43
- [72] Verzera A, Tripodi G, Conduro C, Dima G, Marra A. Chiral volatile compounds for the determination of orange honey authenticity. *Food Control*. 2014;**39**:237-243
- [73] Lercker G, Savioli S, Vecchi MA, Sabatini AG, Nanetti A, Piana L. Carbohydrate determination of Royal Jelly by high resolution gas chromatography (HRGC). *Food Chemistry*. 1986;**19**:255-264

- [74] Ruiz-Matute AI, Soria AC, Sanz ML, Martínez-Castro I. Characterization of traditional Spanish edible plant syrups based on carbohydrate GC-MS analysis. *Journal of Food Composition and Analysis*. 2010B;23:260-263
- [75] Serra Bonvehi J, Orantes Bermejo FJ. Detection of adulterated commercial Spanish beeswax. *Food Chemistry*. 2012;132:642-648
- [76] Maia M, Nunes FM. Authentication of beeswax (*Apis mellifera*) by high-temperature gas chromatography and chemometric analysis. *Food Chemistry*. 2013;136:961-968
- [77] Cheng H, Qin ZH, Guo XF, Hu XS, Wu JH. Geographical origin identification of propolis using GC-MS and electronic nose combined with principal component analysis. *Foodservice Research International*. 2013;51:813-822
- [78] Silva P, Freitas J, Silva CL, Perestrelo R, Nunes FM, Camara JS. Establishment of authenticity and typicality of sugarcane honey based on volatile profile and multivariate analysis. *Food Control*. 2017;73:1176-1188
- [79] Fontecha J, Díaz V, Fraga MJ, Juárez M. Triglyceride analysis by gas chromatography in assessment of authenticity of goat milk fat. *Journal of the American Oil Chemists' Society*. 1998;75:1893-1896
- [80] Collomb M, Butikofer U, Sieber R, Jeangros B, Bosset J-O. Composition of fatty acids in cow's milk fat produced in the lowlands, mountains and highlands of Switzerland using high-resolution gas chromatography. *International Dairy Journal*. 2002;12:649-659
- [81] Destailats F, de Wispelaere M, Joffre F, Golay P-A, Hug B, Giuffrida F, et al. Authenticity of milk fat by fast analysis of triacylglycerols. Application to the detection of partially hydrogenated vegetable oils. *Journal of Chromatography. A*. 2006;1131:227-234
- [82] Povolo M, Pelizzola V, Contarini G. Directly resistively heated-column gas chromatography for the evaluation of cow milk fat purity. *European Journal of Lipid Science and Technology*. 2008;110:1050-1057
- [83] Gutiérrez R, Vega S, Díaz G, Sánchez J, Coronado M, Ramírez A, et al. Detection of non-milk fat in milk fat by gas chromatography and linear discriminant analysis. *Journal of Dairy Science*. 2009;92:1846-1855
- [84] Molkenin J. The effect of cheese ripening on milkfat composition and the detection of fat from non-dairy origin. *International Dairy Journal*. 2013;33:16-21
- [85] Park J-M, Kim N-K, Yang C-Y, Moon K-W, Kim J-M. Determination of the authenticity of dairy products on the basis of fatty acids and triacylglycerols content using GC analysis. *Korean Journal of Food Science and Analysis*. 2014;34:316-324
- [86] Butler G, Stergiadis S, Seal C, Eyre M, Leifert C. Fat composition of organic and conventional retail milk in Northeast England. *Journal of Dairy Science*. 2011;94:24-36
- [87] Capuano E, Gravink R, Boerrigter-Eenling R, van Ruth SM. Fatty acid and triglycerides profiling of retail organic, conventional and pasture milk: Implications for health and authenticity. *International Dairy Journal*. 2015;42:58-63
- [88] Schwendel BH, Morel PCH, Wester TJ, Tavendale MH, Deadman C, Fong B, et al. Fatty acid profile differs between organic and conventionally produced cow milk independent of season or milking time. *Journal of Dairy Science*. 2015;98:1411-1425

- [89] Smiddy MA, Huppertz T, van Ruth SM. Triacylglycerol and melting profiles of milk fat from several species. *International Dairy Journal*. 2012;**24**: 64-69
- [90] Werteker M, Huber S, Kuchling S, Rossmann B, Schreiner M. Differentiation of milk by fatty acid spectra and principal component analysis. *Measurement*. 2017;**98**:311-320
- [91] Pillonel L, Collomb M, Tabacchi M, Bosset JO. Analytical methods for the determination of the geographic origin of Emmental cheese. Free fatty acids, triglycerides and fatty acid composition of cheese fat. *Mitteilungen aus Lebensmitteluntersuchung und Hygiene*. 2002;**93**:217-231
- [92] Pillonel L, Ampuero S, Tabacchi R, Bosset JO. Analytical methods for the determination of the geographic origin of Emmental cheese: Volatile compounds by GC/MS-FID and electronic nose. *European Food Research and Technology*. 2003;**216**: 179-183
- [93] Boscaini E, van Ruth S, Biasioli F, Gasperi F, Mark TD. Gas chromatography-olfactometry (GC-O) and proton transfer reaction-mass spectrometry (PTR-MS) analysis of the flavor profile of Grana Padano, Parmigiano Reggiano, and Grana Trentino cheeses. *Journal of Agricultural and Food Chemistry*. 2003;**51**:1782-1790
- [94] Fontecha J, Mayo I, Toledano G, Juarez M. Triacylglycerol composition of protected designation of origin cheeses during ripening. Authenticity of milk fat. *Journal of Dairy Science*. 2006; **89**:882-887
- [95] Florence ACR, Béal C, Silva RC, Bogsan CSB, Pilleggi ALOS, Gioielli LA, et al. Fatty acid profile, trans-octadecenoic,  $\alpha$ -linolenic and conjugated linoleic acid contents differing in certified organic and conventional probiotic fermented milks. *Food Chemistry*. 2012;**135**:2207-2214
- [96] Marseglia A, Caligiani A, Comino L, Righi F, Quarantelli A, Palla G. Cyclopropyl and  $\alpha$ -cyclohexyl fatty acids as quality markers of cow milk and cheese. *Food Chemistry*. 2013;**140**: 711-716
- [97] Kurz C, Carle R, Schieber A. Characterisation of cell wall polysaccharide profiles of apricots (*Prunus armeniaca* L.), peaches (*Prunus persica* L.), and pumpkins (*Cucurbita* sp.) for the evaluation of fruit product authenticity. *Food Chemistry*. 2008; **106**:421-430
- [98] Schmarr H-G, Bernhardt J. Profiling analysis of volatile compounds from fruits using comprehensive two-dimensional gas chromatography and image processing techniques. *Journal of Chromatography. A*. 2010;**1217**:565-574
- [99] del Castillo MLR, Dobson G. Varietal differences in terpene composition of blackcurrant (*Ribes nigrum* L) berries by solid phase microextraction/gas chromatography. *Journal of the Science of Food and Agriculture*. 2002;**82**:1510-1515
- [100] Pontes M, Marques JC, Câmara JS. Headspace solid-phase microextraction-gas chromatography quadrupole mass spectrometric methodology for the establishment of the volatile composition of *Passiflora* fruit species. *Microchemical Journal*. 2009;**93**:1-11
- [101] Tamborra P, Esti M. Authenticity markers in *Aglianico*, *Uva di Troia*, *Negroamaro* and *Primitivo* grapes. *Analytica Chimica Acta*. 2010;**660**: 221-226
- [102] Aprea E, Gika H, Carlin S, Theodoridis G, Vrhovsek U, Mattivi F. Metabolite profiling on apple volatile content based on solid phase microextraction and gas-chromatography

time of flight mass spectrometry. *Journal of Chromatography. A.* 2011; **1218**:4517-4524

[103] Ghaste M, Narduzzi L, Carlin S, Vrhovsek U, Shulaev V, Mattivi F. Chemical composition of volatile aroma metabolites and their glycosylated precursors that can uniquely differentiate individual grape cultivars. *Food Chemistry.* 2015;**188**:309-319

[104] Cheng H, Chen J, Li X, Pan J, Xue SY, Liu D, et al. Differentiation of the volatile profiles of Chinese bayberry cultivars during storage by HS-SPME-GC/MS combined with principal component analysis. *Postharvest Biology and Technology.* 2015a;**100**: 59-72

[105] Cheng H, Chen J, Chen S, Wu D, Liu D, Ye X. Characterization of aroma-active volatiles in three Chinese bayberry (*Myrica rubra*) cultivars using GC-MS-olfactometry and an electronic nose combined with principal component analysis. *Foodservice Research International.* 2015b;**72**:8-15

[106] Porto-Figueira P, Freitas A, Cruz CJ, Figueira J, Câmara JC. Profiling of passion fruit volatiles: An effective tool to discriminate between species and varieties. *Foodservice Research International.* 2015;**77**:408-418

[107] Khakimov B, Mongi RJ, Sørensen KM, Ndabikunze BK, Chove BE, Engelsen SB. A comprehensive and comparative GC-MS metabolomics study of nonvolatiles in Tanzanian grown mango, pineapple, jackfruit, baobab and tamarind fruits. *Food Chemistry.* 2016;**213**:691-699

[108] Mesquita PRR, Nunes EC, dos Santos FN, Bastos LP, MAPC C, de Rodrigues MF, et al. Discrimination of *Eugenia uniflora* L. biotypes based on volatile compounds in leaves using HS-SPME/GC-MS and chemometric

analysis. *Microchemical Journal.* 2017; **130**:79-87

[109] Khalil MNA, Fekry MI, Farag MA. Metabolome based volatiles profiling in 13 date palm fruit varieties from Egypt via SPME GC-MS and chemometrics. *Food Chemistry.* 2017;**217**:171-181

[110] Cuevas FJ, Moreno-Rojas JM, Ruiz-Moreno MJ. Assessing a traceability technique in fresh oranges (*Citrus sinensis* L. Osbeck) with an HS-SPME-GC-MS method. Towards a volatile characterisation of organic oranges. *Food Chemistry.* 2017;**221**: 1930-1938

[111] Wang D, Duan CQ, Shi Y, Zhu BQ, Javed HU, Wang J. Free and glycosidically bound volatile compounds in sun-dried raisins made from different fragrance intensities grape varieties using a validated HS-SPME with GC-MS method. *Food Chemistry.* 2017;**228**:125-135

[112] Zhang H, Xie Y, Liu C, Chen S, Hu S, Xie Z, et al. Comprehensive comparative analysis of volatile compounds in citrus fruits of different species. *Food Chemistry.* 2017;**230**: 316-326

[113] Giannetti V, Mariani MB, Mannino P, Marini F. Volatile fraction analysis by HS-SPME/GC-MS and chemometric modeling for traceability of apples cultivated in the Northeast Italy. *Food Control.* 2017;**78**: 215-221

[114] Chen Q, Song J, Bi J, Meng X, Wu X. Characterization of volatile profile from ten different varieties of Chinese jujubes by HS-SPME/GC-MS coupled with E-nose. *Foodservice Research International.* 2018;**105**: 605-615

[115] Nijssen LM, Maarse H. Volatile compounds in black currant products: An additional factor in authenticity

control of fruit juices. *Flavour and Fragrance Journal*. 1986;**1**:143-148

[116] Low NH. Determination of fruit juice authenticity by capillary gas chromatography with flame ionization detection. *Journal of AOAC International*. 1996;**79**:724-737

[117] Del Castillo MLR, Caja MM, Herraiz M. Use of the enantiomeric composition for the assessment of the authenticity of fruit beverages. *Journal of Agricultural and Food Chemistry*. 2003;**51**:1284-1288

[118] Reinhard H, Sager F, Zoller O. Citrus juice classification by SPME-GC-MS and electronic nose measurements. *LWT- Food Science and Technology*. 2008;**41**:1906-1912

[119] Cuevas FJ, Pereira-Caro G, Moreno-Rojas JM, Munoz-Redondo JM, Ruiz-Moreno MJ. Assessment of premium organic orange juices authenticity using HPLC-HR-MS and HS-SPME-GC-MS combining data fusion and chemometrics. *Food Control*. 2017;**82**:203-211

[120] Armanino C, De Acutis R, Festa MR. Wheat lipids to discriminate species, varieties, geographical origins and crop years. *Analytica Chimica Acta*. 2002;**454**:315-326

[121] Pelillo M, Iafelice G, Marconi E, Caboni MF. Identification of plant sterols in hexaploid and tetraploid wheats using gas chromatography with mass spectrometry. *Rapid Communications in Mass Spectrometry*. 2003;**17**:2245-2252

[122] Tres A, Heenan SP, van Ruth S. Authentication of dried distilled grain with solubles (DDGS) by fatty acid and volatile profiling. *LWT- Food Science and Technology*. 2014;**59**:215-221

[123] Pastor K, Ačanski M, Vujić D, Bekavac G, Milovac S, Kravić S. Rapid

method for small grain and corn flour authentication using GC/EI-MS and multivariate analysis. *Food Analytical Methods*. 2016a;**8**:443-450

[124] Pastor K, Acanski M, Vujic D, Kondic-Špika A. Binary simple sugar profiling in corn and small grain flour authentication using GC/EI-qMS approach. *Chromatographia*. 2016b;**79**:1553-1559

[125] Pastor K, Acanski M, Vujic D, Jovanovic D, Wienkoop S. Authentication of cereal flours by multivariate analysis of GC-MS data. *Chromatographia*. 2016c;**79**:1387-1393

[126] Pastor K, Pezo L, Vujić D, Jovanović D, Ačanski M. Discriminating cereal and pseudocereal species using a binary system of GC-MS data—A pattern recognition approach. *Journal of the Serbian Chemical Society*. 2018;**83**:317-329

[127] Psodorov Đ, Vujić D, Ačanski M, Pastor K, Razmovski R, Kravić S. The content of buckwheat flour in wheat bread. *Acta Periodica Technologica*. 2014;**45**:79-87

[128] Psodorov D, Ačanski M, Psodorov D, Vujić D, Pastor K. Determination of the content of buckwheat and wheat flours in bread using GC-MS and multivariate analysis. *Journal of Food and Nutrition Research*. 2015;**54**:179-183

[129] Zhang Z, Li T, Wang D, Zhang L, Chen G. Study on the volatile profile characteristics of oyster *Crassostrea gigas* during storage by a combination sampling method coupled with GC/MS. *Food Chemistry*. 2009;**115**:1150-1157

[130] Iglesias J, Medina I, Bianchi F, Careri M, Mangia A, Musci M. Study of the volatile compounds useful for the characterisation of fresh and frozen-thawed cultured gilthead sea bream fish by solid-phase microextraction gas

chromatography-mass spectrometry.  
Food Chemistry. 2009;**115**:1473-1478

[131] Zhang Z, Li G, Luo L, Chen G. Study on seafood volatile profile characteristics during storage and its potential use for freshness evaluation by headspace solid phase microextraction coupled with gas chromatography-mass spectrometry. *Analytica Chimica Acta*. 2010;**659**:151-158

[132] van Houcke J, Medina I, Linssen J, Luten J. Biochemical and volatile organic compound profile of European flat oyster (*Ostrea edulis*) and Pacific cupped oyster (*Crassostrea gigas*) cultivated in the Eastern Scheldt and Lake Grevelingen, the Netherlands. *Food Control*. 2016;**68**:200-207

[133] Nurjuliana M, Che Man YB, Mat Hashim D, Mohamed AKS. Rapid identification of pork for halal authentication using the electronic nose and gas chromatography mass spectrometer with headspace analyzer. *Meat Science*. 2011;**88**:638-644

[134] Gorska-Horczyzak E, Horczyzak M, Guzek D, Wojtasik-Kalinowska I, Wierzbicka A. Chromatographic fingerprints supported by artificial neural network for differentiation of fresh and frozen pork. *Food Control*. 2017;**73**:237-244

[135] Rui Alves M, Casal S, Oliveira MBPP, Ferreira MA. Contribution of FA profile obtained by high-resolution GC/chemometric techniques to the authenticity of green and roasted coffee varieties. *JAOCS*. 2003;**80**:511-517

[136] Risticvic S. HS-SPME-GC-TOFMS methodology for verification of geographical origin and authenticity attributes of coffee samples [thesis]. Ontario, Canada: Waterloo; 2008

[137] Lienert D, Anklam E, Panne U. Gas chromatography-mass spectral analysis

of roots of *Echinacea* species and classification by multivariate data analysis. *Phytochemical Analysis*. 1998; **9**:88-98

[138] Lin J, Zhang P, Pan Z, Xu H, Luo Y, Wang X. Discrimination of oolong tea (*Camellia sinensis*) varieties based on feature extraction and selection from aromatic profiles analysed by HS-SPME/GC-MS. *Food Chemistry*. 2013; **141**:259-265

[139] Farag M, Rasheed DM, Kamal IM. Volatiles and primary metabolites profiling in two *Hibiscus sabdariffa* (roselle) cultivars via headspace SPME-GC-MS and chemometrics. *Foodservice Research International*. 2015;**78**:327-335

[140] Zhu Y, Shao C-Y, Lva H-P, Zhang Y, Dai W-D, Guo L, et al. Enantiomeric and quantitative analysis of volatile terpenoids indifferent teas (*Camellia sinensis*). *Journal of Chromatography. A*. 2017;**1490**:177-190

[141] Cui S, Wu J, Wang J, Wang X. Discrimination of American ginseng and Asian ginseng using electronic nose and gas chromatography mass spectrometry coupled with chemometrics. *Journal of Ginseng Research*. 2017;**41**:85-95